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CONTENTS

135 : 9

TRANSACTIONS

PAGE

"SOIL MOISTURE IN RELATION TO MOISTURE IN THE SURFACE LAYERS OF THE ATMOSPHERE DURING THE CLEAR SEASON" M. S. KATTI 3
MEASUREMENT OF AIR-EARTH CURRENTS PASSING THROUGH ELEVATED POINTS DURING ELECTRICALLY DISTURBED WEATHER AT COLABA, BOMBAY M. W. CHIPLONKAR 9
THE DUST-FREE OR DARK LAYER SURROUNDING A HOT BODY IN RELATION TO THE CONVECTIVE MOVEMENTS IN ITS NEIGHBOURHOOD L. A. RAMDAS 18
"BEAM" AMPLIFIER B. B. DESHPANDE 23
THE STUDY OF THE OXY-COALGAS FLAME BY BAND SPECTRA . N. R. TAWADE AND J. M. PATEL 29
MUTUAL COAGULATION OF COLLOIDAL SOLUTIONS PART I—INTERACTION OF FERRIC HYDROXIDE AND PRUSSIAN BLUE SOLS P. M. BARVE, Y. S. PARANJPE AND B. N. DESAI 50
THE ACTION OF NITRIC ACID ON MERCURY—PART I MADHAVLAL SUKHLAL SHAH AND BHASKER GOVIND JOSHI 57
STUDY OF A REACTION BETWEEN AQUEOUS SOLUTIONS OF MERCURIC CHLORIDE AND DISODIUM HYDROGEN PHOSPHATE S. M. MEHTA AND S. M. SHETH 75
SOME REACTIONS OF OXANILIDE-DI-IMIDOCHLORIDE (DIPHENYL-OXAL-IMIDOCHLORIDE) V. R. HEERAMANECK AND R. C. SHAH 80
THE ACTION OF THIONYL CHLORIDE AND SULPHUR DI-CHLORIDE ON METHYL SALICYLATE J. A. KUNDARGI, Y. M CHAKRADEO AND S. V. SHAH 82
THE CONDENSATION OF ARYLAMINES WITH THE CYANOHYDRINE OF R CAMPHOR AND 3-METHYL-CYCLOPANTANONE R. D. DESAI, AHMAD KAMAL AND S. ALI NOMIN 85
HETEROCYCLIC COMPOUNDS PART VI COUMARINS FROM ETHYL - β - CHLOROPROPYLACETOACETATE AND THE MERCURATION OF COUMARINES FROM ETHYLCYCLOHEXANONE 2-CARBOXYLATE S. ZAFARUDDIN AHMAD AND R. D. DESAI 89
SYNTHESIS IN THE CHAULMOOGRIC ACID SERIES :—PART I. A NEW SYNTHESIS OF DIHYDROHYDNOCARPIC ACID K. V. BOKIL AND K S. NARGUND 93
CONSTITUTION AND DERIVATIVES OF α PHENYL GLUTACONIC ACID N. L. PHALNIKAR AND K. S. NARGUND 97
PHENYLGLUTARIC ACIDS PART II. β-PHENYL-β-METHYL GLUTARIC ACID N. L. PHALNIKAR AND K. S. NARGUND 102

A NOTE OF CRITICISM ON THE SYNTHESIS BY DIXIT OF β P-HYDROXY (OR P-METHOXY) - PHENYLGLUTACONIC ACID FROM THE CORRESPONDING GLUTARIC ACID .. ..N. L. PHALNIKAR AND K. S. NARGUND 104

FLAVONE DERIVATIVES FROM GLYCEROL ETHERS OF RESACETOPHENONE .. .. D. R. NADKARNI AND T. S. WHEELER 107

REACTIVITY OF FORMIC ACID :—A METHOD OF ESTIMATING SIDE-CHAIN HALOGEN IN AROMATIC COMPOUNDS .. .. (Miss) K. D. GAVANKAR, L. S. HEBLE AND T. S. WHEELER 112

CONDENSATION OF CHLORAL WITH URETHANES : A STUDY OF THE GROUP NH. CHOH.C.Cl_3 .. .. (The Late) A. N. MELDRUM AND D. B. PANDYA 114

NUCLEAR CONDENSATION PRODUCTS OF CHLORAL WITH PHENOLS .. .. (The Late) A. N. MELDRUM AND K. V. LONKAR 116

A NOTE ON THE REDUCTION OF SOME DERIVATIVES OF ANHYDRO-2 - βββ-TRICHLORO-α-HYDROXYETHOXY-1-βββ-TRICHLORO-α-HYDROXY-ETHYL-BENZENE .. (The Late) A. N. MELDRUM AND A. S. TATA 120

STUDIES IN CHLORAL-AMIDES—PART IV. REACTIVITY OF α-OH GROUP IN CHLORAL-NITRO-SALICYLAMIDES N. W. HIRWE AND (Miss) K. D. GAVANKAR 123

DERIVATIVES OF N-PHENYLBENZAMIDINE : PART I. .. H. P. GHADIALI AND R. C. SHAH 127

PHOSPHORYL CHLORIDE AS A CONDENSING AGENT IN THE PREPARATION OF AMIDINES FROM ACYLAMINES M. M. SIDIKI AND R. C. SHAH 132

PRODUCTION OF TERPINEOL FROM PINENE .. .. B. G. S. ACHARYA AND T. S. WHEELER 134

STUDY OF SOME PHYSICAL PROPERTIES OF COMMERCIAL GUMS .. .. N. A. YAJNIK, P. L. KAPUR AND MANPHUL SINGH JAIN 136

A COMPARISON OF THE OILS FROM THE LOCAL AND 104 SPANISH VARIETIES OF GROUND-NUT .. .. .. W. V. KOTASTHANE AND N. NARAYANA 143

ARTICLES

A NOTE ON MAXIMA AND MINIMA .. K. R. GUNJIKAR 148

PROPAGATION OF LIGHT WAVES THROUGH ETHER .. L. V. GURJAR 149

SOLUTION OF THE BERNOULI-EULERIAN THEOREM ON BENDING OF RODS .. .. .. L. V. GURJAR 155

THEORY OF MAGNETISM—(A SUMMARY) .. .. .. K. R. DIXIT 160

THE CHEMICAL CONSTITUTION OF THE SEX HORMONES —A SURVEY OF RECENT WORK .. D. D. KARVE 171

CHEMISTRY OF CHLORAL AND CHLORAL HYDRATE .. N. W. HIRWE 182

ABSTRACTS OF THESES 199

NOTES AND NEWS 208

REVIEWS 211

BOOKS RECEIVED 213

ACKNOWLEDGMENTS 215

EXCHANGES 216

"SOIL MOISTURE IN RELATION TO MOISTURE IN THE SURFACE LAYERS OF THE ATMOSPHERE DURING THE CLEAR SEASON" *

By

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1. *Introduction.*

It is well known that many objects in nature like wood, hair, fibres, soils etc. are hygroscopic i.e., they give up a certain amount of water vapour if heated or otherwise desiccated and absorb moisture if exposed again to a humid atmosphere.

Recent investigations (1, 2, 3, 4) at Poona during the last two and half years have shown that the hygroscopic properties of the soil at the earth's surface have a meteorological significance so far as the exchange of water vapour between the soil and the air layers near it during dry weather is concerned. These investigations included a study of the behaviour of soils from different parts of the country when exposed simultaneously to identical weather conditions and also of the physical properties of these soils. It may be mentioned that throughout the investigation the meteorological aspect was kept in the fore-front and the soils were used as they occur i.e., without separating them into their components by mechanical or chemical analysis.

The experiments were done during the dry season (November-April) which is characterised by a simple climate of the continental type over the Bombay Deccan, with more or less clear skies, feeble winds and large diurnal variation of temperature.

During this period the surface of the ground is subjected to intense heating during the day. It may therefore be expected that the surface soil may be so desiccated under these circumstances that it retains only the minimum of water consistent with its hygroscopic properties. Actual measurements show that the water content of the soil at all depths is large during the monsoon months and that there is a rapid desiccation of the upper layers after the withdrawal of the monsoon. It is, however, very significant that even after the intense desiccation during the winter, spring and summer months the moisture content of the soil at depths of 1 foot and more is still as high as 30%.

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* Summary of thesis submitted for the M. Sc., degree of the Bombay University.

We shall see later how the dry mulch at the top of the soil acts as a protecting layer and checks the loss of moisture from the interior of the soil.

2. *The variation of the water vapour content of the air layers near the ground with height.*

The daily psychometric measurements at the Central Agricultural Meteorological Observatory at Poona show that at the epoch of maximum temperature during the clear season the pressure of water vapour is maximum near the ground and decreases with height. Comparing the values near the soil surface with those at 10 ft. above ground, the decrease of water content is on the average about 25 % of the mean value for the 10 ft. layer. The degree of saturation of the air with water vapour increases with height. This is easily understood because the dry bulb temperature is very high near the ground at the maximum temperature epoch.

Again it is found that at the epoch of minimum temperature the conditions are reversed so far as the pressure of water vapour is concerned. The water vapour content is now least near the ground and increases with height, the average increase from ground level to 10 ft. being again of the order of 25%. In this case also the humidity percentage is minimum near the ground, and increases with height. The lower values of both the pressure and degree of saturation of water vapour very near the ground considered together with the temperature gradients which are feebler than those in the afternoon, show that the results obtained at the minimum temperature epoch are not easy to understand unless the soil surface acts like a desiccating agent during the night. The reversal in the vertical gradient of vapour pressure was somewhat puzzling at first and attempts were actually made to discover whether the phenomenon was due to the settling down of drier air from above which may have cooled more than the air layers near the ground by radiative processes. As soon as experiments were begun with soil samples to investigate any possible influence of the soil itself it became rapidly evident that the real cause of the phenomenon has to be sought for in that direction.

3. *Moisture content of soil in the morning and afternoon.*

Daily measurements of the moisture contents of soil samples exposed in small vessels as well as from the surface of the actual field in the morning and afternoon showed that the soil has much more moisture in the morning than in the afternoon. Such samples did not show any progressive loss of water, indicating that what is lost by evaporation during the day is regained from the atmosphere during the night.

4. *Hourly variations of the water content of the surface layers of the soil.*

Hourly determination of the water content of soil samples exposed to the sky show that the soils have their minimum moisture content about the epoch of maximum temperature and their maximum moisture content at the epoch of minimum temperature.

It is significant that the variation of moisture content of the soil is in phase with the variation of the air temperature and the percentage humidity rather than the soil surface temperature (which closely follows the altitude of the sun and has a maximum value when the sun is over-head.).

The soil samples weighed 60 grammes each and were exposed in vessels whose area of cross section was 30 sq cm. It is found that the black cotton soils undergo the maximum diurnal variation of moisture content of the order of 2 grammes owing to the loss of water by evaporation during the day and gain by absorption from the air during the night The red soils come next with a variation of about 1½ gr. The alluvial soils from the Indo-Gangetic as well as the Sind areas show a diurnal variation which is only a fifth of that of the black cotton soils. The sample of quartz powder comes at the bottom of the list with no variation It is indeed remarkable that soils from places at large distances apart show very similar features so long as they belong to the same soil group

The amplitude of the diurnal variation in the moisture contents of different soils expressed as a ratio of that of the Poona soil are given below :—

Name of soil	Diurnal variation of moisture content expressed in terms of Poona soil (= 1).
Poona black cotton soil	1·00
Dharwar black cotton soil	1·10
Sholapur black soil	1·04
Hagari	0·86
Red Laterite	0·81
Ranchi	0·65
Jhelum	0·44
Bangalore	0·29
Pusa (alluvial)	0·20
Lyallpur (alluvial)	0·21
Sakrand (alluvial)	0·19
Quartz powder	0·00

The hourly variation of the moisture content of the Poona soil at different depths has also been studied by taking actual hourly samples from the field and determining their moisture contents. It is seen that the diurnal variation is maximum at the surface and decreases very rapidly with depth, being practically insignificant even at a depth of 1″ below the surface.

5. *The "moisture-variation-index" in relation to other important physical properties of the soil.*

The sequence of the moisture variation indices of different soils as observed in the open is practically the same as that of their power to absorb water vapour when exposed under known conditions of temperature and humidity in the laboratory.

The water-holding capacities of a few soils (expressed on air-dry basis) are given below :—

Soil	Water-holding capacity
Poona.	38·7 %
Sholapur	41·0 „
Hagari	30·9 „
Bangalore	24·0 „
Pusa	26·2 „
Lyallpur	22·8 „

The black cotton group of soils is able to retain 15% more of water than the alluvial group.

The values of the heat of wetting at 25·9°C for different soils run parallel to those of the moisture-variation-index, being large for the black cotton soils and small for the alluvial soils as may be seen from the table below,—

Name of soil	Heat of wetting per gramme of soil in gramme calories at 25·9°C
Poona	8·7
Ranchi	4·8
Jhelum	2·2
Pusa	1·2

In determining the moisture content of a soil, the sample is usually kept in the steam oven "till the weight becomes constant." An exact study of the rate of drying in a steam oven is very instructive. The weight-time curves for four typical soils starting with about 100% water (on dry basis) not only show the time for complete drying but also the rate of drying at different moisture contents. The times taken by different soils for attaining a steady minimum weight at 100°C are in the same order as their moisture-variation-indices.

The similarity in the behaviour of a number of physical properties of different soils to their moisture-variation-indices is striking.

6. *Soils as desiccating agents.*

The efficiency of different soils as desiccating agents under steady conditions in the laboratory was also measured. The method adopted was to pass an air current (whose initial humidity was known) above the dried soil and to note the decrease of humidity after passage.

These experiments were performed with four soils viz. soils from Poona, Jalgaon, Bangalore and Lyallpur. For comparing the desiccating power of these soils with that of a standard substance the experiment was also repeated with a sample of " Sorbsil " supplied by the Cambridge Instrument Company.

The velocity of the air current is adjusted so as to allow 43·8 cc. of air per second to pass through the apparatus. After passage above the soil exposed in the drying tube the wet bulb temperature rapidly falls in the first few minutes and slowly rises again. Each experiment was concluded as soon as the air current ceased to be desiccated i.e., as soon as the soil had got exhausted and no longer absorbed any moisture from the air current. When this stage was reached the humidity of the air current was practically identical with that of the room air outside the apparatus.

Sorbsil is an efficient absorber, and retains its power to absorb for the longest time. Next in order come the soils from Poona, Jalgaon, Bangalore and Lyallpur respectively. The last two cause only a small depression in the wet bulb temperature and the vapour pressure and get exhausted within 10 minutes. In all cases the dehydration of the air current is rapid and the vapour pressure attains its minimum value within a few minutes after the commencement of the experiment ; thereafter the vapour pressure slowly increases and becomes equal to that of the air outside.

These results suggest that the black cotton soils may be used with profit for keeping the air in an enclosed space dry. The cost involved would be negligible when compared to that of common drying agents like sulphuric acid, calcium chloride, phosphorous pentoxide, etc.

Conclusion.

These investigations were made at the Meteorological Office at Poona under the guidance of Dr. L. A. Ramdas to whom the author's best thanks are due.

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MEASUREMENT OF AIR-EARTH CURRENTS PASSING THROUGH ELEVATED POINTS DURING ELECTRICALLY DISTURBED WEATHER AT COLABA, BOMBAY.

By

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Introduction.—The potential gradient at the earth's surface is normally positive, which implies that the earth's surface is ordinarily negatively charged. Owing to this normal electric field, positive ions are continually being drawn into the earth thus giving rise to the fine-weather Air-Earth current. One of the most fundamental problems of Atmospheric Electricity is to account for the maintenance of the negative charge on the earth's surface. Prof. C. T. R. Wilson[1] first suggested that point discharges from tall objects like trees, house tops, mountain peaks etc. under the influence of the strong electric fields of a thunder-cloud would cause a negative air-earth current which would thus maintain the earth's negative charge. Since then there have been a few investigations on this type of interchange of electricity between the earth and the atmosphere. T W. Wormell[2] measured at Cambridge the total amount of discharge from a raised metal point for a period of three years. He used a specially designed water-voltameter to measure the total amount of charge passing in or out of the metal point during long intervals of time. The point discharge current during disturbed conditions was measured separately by charging a condenser connected across a spark gap in the point discharge circuit. Schonland[3] in South Africa employed a small tree cut off at its base and mounted on insulators in an open space to measure the point discharge. The current passing through the tree was measured by means of a galvanometer, the other end of which was earthed. Whipple and Scrase[4] have published their results of point discharge currents recorded at Kew during the period July 1932 to December 1934. They used a single point discharger similar to that used by Wormell but connected directly to a galvanometer. This same arrangement was used at Colaba, to measure the point discharge current during the post monsoon months of 1936.

Prof. C. T. R. Wilson's suggestion includes three processes occurring in disturbed weather by which a transfer of electric charge may take place between the earth and the atmosphere. They are :—

(i) Momentary currents due to lightning.

(ii) Precipitation currents carried by water drops during rain, fog, mist, etc.

(iii) Continuous currents carried by ions moving under the action of the strong electric fields of thunderclouds.

Schonland's[3] estimates have shown that the last named process plays the main role while the other two are comparatively much less important. The following is an account of some measurements of point discharge currents made at Colaba during thunderstorms in September and October of 1936.

Afternoon thunderstorms :—The two months of September and October, the period of our observations, are marked in Bombay by a change in the direction of the prevailing winds over the west coast of the Indian Peninsula. The moist south-west monsoon winds give place to the drier land winds which come from northwest India. During this period of transition afternoon thunderstorms are frequent. At Bombay thunderclouds usually appear in the afternoon towards North-East or East of the Observatory over the neighbouring Indian coast and travel towards South-East or South. Oftentimes they develop into strong thunderstorms late in the afternoon and gradually travel over the island of Bombay. However during the last year very few of them directly passed over the Observatory at Colaba. The only occasion when it did so was on 22nd September, 1936.

EXPERIMENTAL ARRANGEMENT FOR THE POINT DISCHARGE CURRENT

A photograph of the point discharger and its surroundings is shown in fig. 1. The discharging system is similar to that used by Wormell and is shown diagrammatically in fig. 2. The actual height of the metal point above the ground level was 7·4 m. It was connected by means of a lead-covered rubber insulated cable to a moving coil galvanometer having a resistance of 15·7 ohms and a current sensitivity of $2{\cdot}0 \times 10^{-8}$ amps. per mm. Eye-observations of point discharge currents flowing through the galvanometer were made with the usual lamp and scale arrangement. The sulphur insulation at the top was always scraped and kept free from moisture and insects etc. It was examined every time before taking a measurement.

Exposure :—The mast carrying the discharging system is situated at a distance of about 13 metres from the surrounding low buildings. The lead-covered wire is brought down along the mast to a height of 4 metres and then taken overhead to the ceiling of a

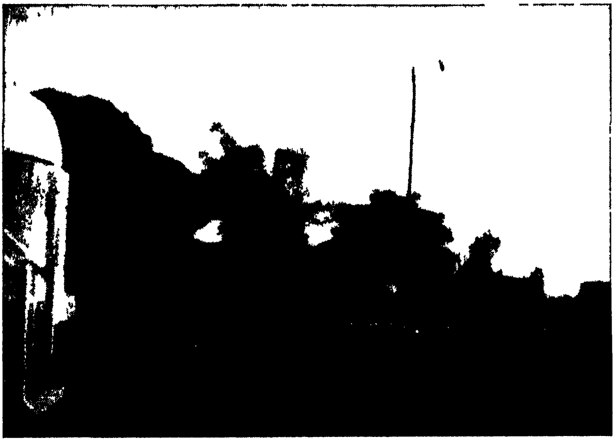
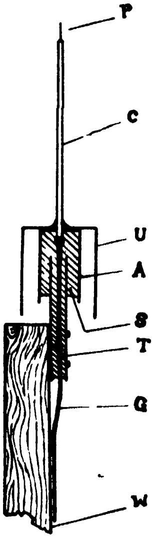


FIG. 1.- Point Discharger and its surroundings.



P = Fine copper wire.

C = Stout copper wire.

U = Metal umbrella.

A = Metal can.

S = Sulphur.

T = Brass Tube.

G = Connecting wire.

W = Wooden Mast.

FIG. 2.—Point Discharger.

small old dome-shaped building (seen in the left hand side of the photograph). This has a height of 3·5 metres and is at a distance of 13 m. from the mast. Besides a few trees beyond a distance of 13 m. by far the most disturbing objects in the neighbourhood are the lightning conductor and the rain-gauge funnel on the top of the large thermometer house, both about 8 m. high and 23 m. and 19 m. respectively from the mast. Although the exposure of the discharging system was not very open, preliminary observations were thought worth-while.

The exposure factor of the discharging system was found out in the following manner :—

An ionium collector was suspended by means of sulphur insulators at the end of a wooden cross-piece at the same height as the discharging system and about a metre distant from the main mast. The collector was directly connected to a Dolezalek Electrometer by means of a long thin copper wire. Thus the other conditions of exposure being the same, the ionium collector picked up the actual potential at the top of the point discharger. These measurements were made in the afternoon on clear days when the potential gradient has been found to be steady. Comparisons made on a number of occasions showed that the equivalent height of the point over level ground was 2·6 m. implying an exposure factor of 2·85. It is obvious that the exposure factor of the point is a factor of considerable importance in all measurements of earth-air current.

Experimental Results :—It was possible to record the currents in five thunderstorms which include the only severe one of the season and referred to before. The potential gradient trace and the point discharge current trace for two of them are shown in figs. 3 and 4

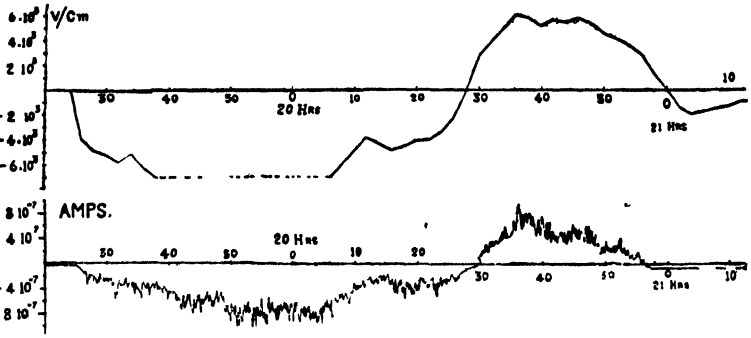


FIG. 3.—Potential Gradient and Point Discharge Current during the thunderstorm of 22nd September, 1936.

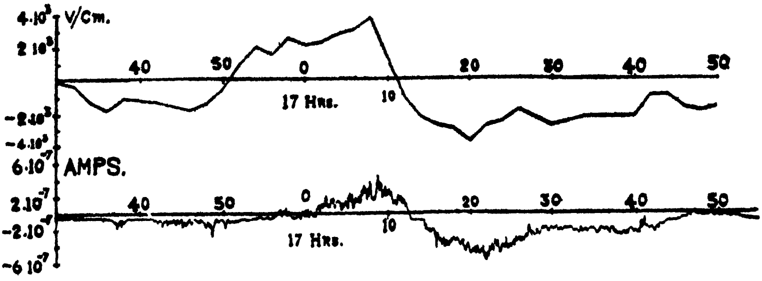


FIG. 4.—Potential Gradient and Point Discharge Current during the thunderstorm of 30th September, 1936.

The potential gradient recorder which working since 1930 at Colaba is at a distance of about 150 metres from the point discharger. The values of potential gradient during thunderstorms were read from these photographic records and plotted on the same time scale as the point discharge current trace. The correspondence between the two traces is striking and shows that the two instruments were affected simultaneously and that their values may be compared without introducing any serious error.

The following table gives the quantities of electricity transferred during each of the thunderstorms.

TABLE I.

Total point discharge during the five thunderstorms observed At Colaba, Bombay.

Effective height of the point above ground level—2·6 m.

Date.	Duration of thunder-storm.	Charge in Millicoulombs.		
		In.	Out.	Nett transfer.
	H. M. to H. M.			
8·9·36	14 15 to 14 46	0·0	0·024	−0·02 (out)
22·9·36	18 35 to 21 20	0·91	1·57	−0·66 (out)
28·9·36	16 28 to 18 0	0·10	0·04	+0·06 (in)
29·9·36	18 10 to 19 15	0·04	0·25	−0·21 (out)
30·9·36	16 0 to 18 5	0·16	0·47	−0·31 (out)

Fig. 5 shows the relation between the potential gradient and the corresponding point discharge current observed during these thunderstorms. For the sake of comparison these results and those obtained by Whipple and Scrase and Schonland are shown together in Fig. 6. Whipple and Scrase's[4] curve (obtained from the records of six thunderstorms at Kew) shows higher values of current for the same field than those obtained at Colaba, while the South African results are lower. This is because of the greater effective height (8 metres) of the point above the ground level at Kew. In the experiments of Schonland although a 4 metre tall tree was used, the effective height would have been much less as the discharging points would be distributed over different heights all under 4 metres.

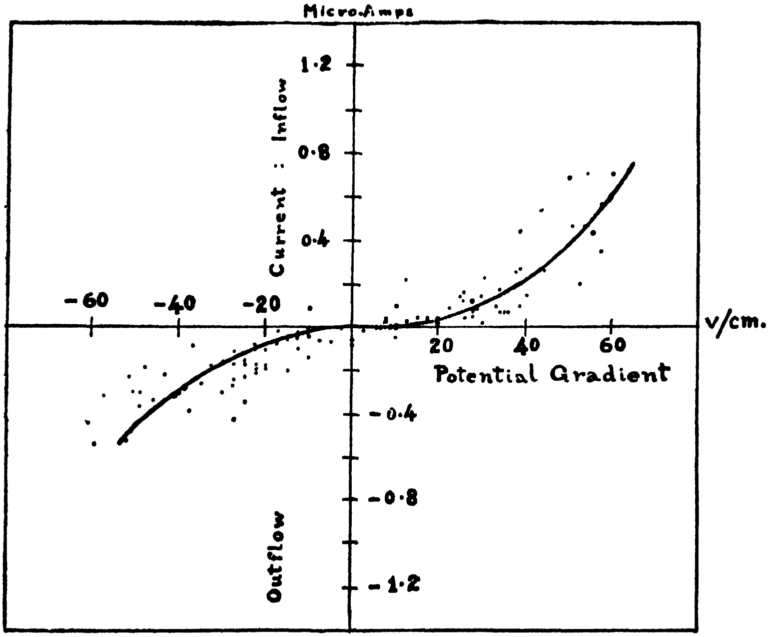


Fig. 5.—Point Discharge Current—Potential Gradient Curve obtained at Colaba, Bombay.

A MINIMUM ESTIMATE OF THE TOTAL TRANSFER OF CHARGE DURING ONE COMPLETE YEAR AT COLABA, BOMBAY

High values of potential gradient are common at Colaba in the months of May and June during thunderstorms. They also occur, though with smaller values, during showers in the monsoon. When such high values of potential gradient prevail, the spot of light would ordinarily go off the photographic paper of the potential gradient recorder. So it is customary at Colaba during disturbed conditions to decrease the magnification in a definite ratio, by drawing in the radioactive collector. Nevertheless, the records on some occasions were

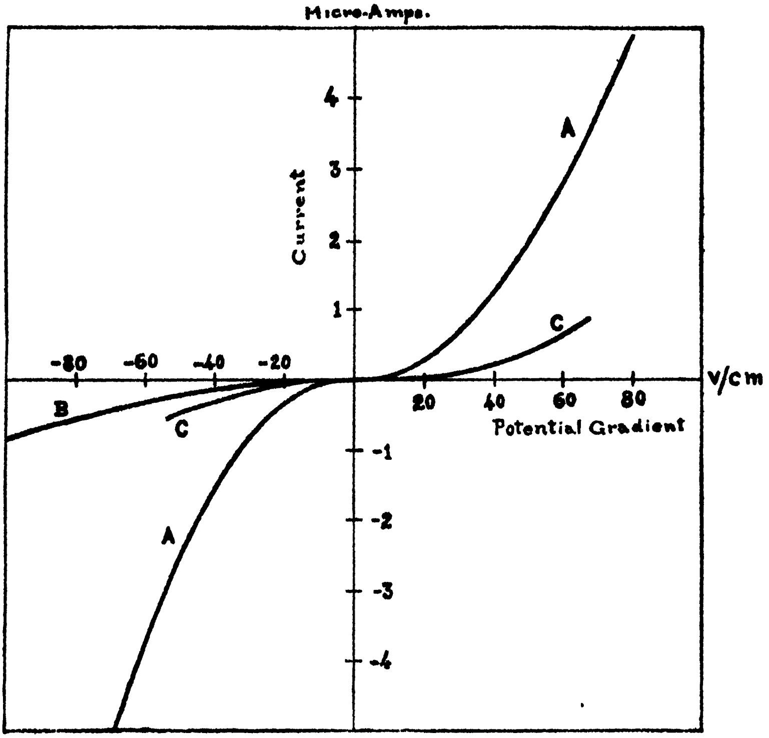


FIG. 6.—Comparison of Point Discharge—Potential Gradient Curves with different height of the Point Discharge.

A = Whipple and Scrase—effective height 8·4 metres.
B = Schonland—effective height L4·0 metres.
C = Author—effective height 2· metres.

lost, the spot of light going out for considerable periods. From the potential gradient records for one complete year (1st November, 1935, to 1st November, 1936), all occasions of high values were picked out and taking Whipple and Scrase's curve as representing current—potential relation when the point is 8 metres above ground level, the point discharge currents were read and the total transfer of charge on each such occasion calculated. On occasions of high field values when the spot of light was within the paper the estimates are unambiguous; but on those occasions when the trace was outside the paper only a minimum value could be estimated. Fortunately the minimum value of the potential gradient at which the point discharge begins, happens to be about the same as that recorded when the spot of light is normally on the edge of the paper. In Table II, are given the results of such calculations for individual unambiguous occasions In Table III, are given the minimum point discharge values summed up for each separate month. The nett transfer of charge from the earth to the air as shown at the bottom of Table II, for the whole year, comes to 9·31 Milli-Coulombs. Assuming a mean air-earth current of 3×10^{-16} amp. per sq. cm. during fine weather, 9·3 milli-coulombs is equal to the quantity of charge that would be conveyed from air to earth during fine weather over a period of one year and from an area of about 100 sq. metres.

TABLE II.

Total Point-Discharge calculated from the high Potential Gradient values recorded at Colaba during the year, 1st November, 1935 to 1st November, 1936, assuming the effective height of the discharging point to be 8 m. and the potential gradient—current relation to be that given by Whipple and Scrase.

Date	Duration of Field		Charge in Milli-Coulombs			
			In	Out	Nett Transfer	
	Hrs.	Mins.				
30-9-36	1	50	0·56	0·93	0·37	(out)
29-9-36	2	12	0·84	0·77	0·07	(in)
28-9-36	1	40	0·28	0·14	0·14	(in)
26-9-36	0	48	0·0	0·85	0·85	(out)
24-9-36	1	10	0·19	0·11	0·08	(in)
22-9-36	3	48	5·98	13·40	7·42	(out)
21-9-36	1	16	0·97	0·52	0·45	(in)
20-9-36	1	8	0·01	0·49	0·48	(out)
8-9-36	0	46	0·04	0·12	0·08	(out)
28-6-36	2	4	0·01	0·0	0·01	(in)
27-6-36	4	6	1·14	1·98	0·84	(out)
26-6-36	0	20	0·0	0·02	0·02	(out)
24-6-36	1	40	0·29	0·46	0·17	(out)
22-6-36	0	22	0·01	0·03	0·02	(out)
21-6-36	0	34	0·31	0·0	0·31	(in)
Sub-Total			10·63	19·82	10·25 1·06	(out) (in)
					9·19	(out)
Total Minimum Estimate from Table III			0·43	0·55	0·12	(out)
Grand Total			11·06	20·37	9·31	(out)

TABLE III.

Minimum estimate of Point-Discharge during the high potential gradients when the spot of light went off the recording paper.

Month.	Sign of the Pot. Gradient.	Total Duration.	Total Point-Discharge.
December 1935	+ve	56 minutes,	0·067 (in)
February 1936	+ve	16 „	0·019 (in)
March „	+ve	50 „	0·06 (in)
	−ve	4 „	0·005 (out)
June „	+ve	20 „	0·024 (in)
	−ve	137 „	0·164 (out)
July „	+ve	30 „	0·036 (in)
	−ve	8 „	0·01 (out)
August „	+ve	21 „	0·025 (in)
	−ve	74 „	0·089 (out)
September „	+ve	44 „	0·053 (in)
	−ve	54 „	0·065 (out)
*	+ve	4 „	0·072 (in)
*	−ve	12 „	0·216 (out)
October „	+ve	63 „	0·076 (in)

Total 0·43 (in)
0·55 (out)

Nett Charge going out—0·12

DISCUSSION

It can easily be seen from Table II, that in a single strong thunderstorm as for example the one that occurred on 22nd September, 1936, at Colaba, the discharge current was so large that the major portion of the annual nett transfer of electric charge from the earth to the air was supplied by it.

In connection with the above experiments it should be noted that the rapid momentary changes in the field and the point discharge currents accompanying lightning flashes cannot be recorded by the instruments used owing to their large period. Such rapid changes are usually measured by the capillary electrometer, or better by Cathode-ray Oscillograph (1), (5), (6), (7). They show definite types of momentary changes of very great magnitude depending upon the intensity and distance of the flash from the place of observation; but owing to their much shorter duration are of less importance for the total transfer of charge from the earth to the air than the comparatively steadier high fields associated with the presence of charged clouds.

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*N.B.—On these occasions the magnification was reduced in the ratio 1 : 2·1.

In order to know the total transfer of charge by a thunderstorm it would be necessary to estimate the area over which it caused appreciable point discharge currents during the time it lasted and the magnitudes of the currents at different places. Simultaneous observations of both the potential gradients and point discharge currents at three or more places a few kilometers apart will doubtless lead to very interesting results.

The author has great pleasure in expressing his sincere thanks to Dr. K. R. Ramanathan, Meteorologist, Bombay, under whose direction the above work was carried in the Colaba Observatory, Bombay, and also to the University of Bombay for giving a research grant.

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THE DUST-FREE OR DARK LAYER SURROUNDING A HOT BODY IN RELATION TO THE CONVECTIVE MOVEMENTS IN ITS NEIGHBOURHOOD

By

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The investigations of Tyndall,[1] Rayleigh,[2] Aitken[3] and Lodge and Clark[4] have shown that, when a hot object is kept in a dusty atmosphere and suitably illuminated, a thin dark or dust-free layer is seen to envelop the hot surface, the thickness increasing at the top where the dust-free layer is seen to ascend like a pillar (Fig. 1).

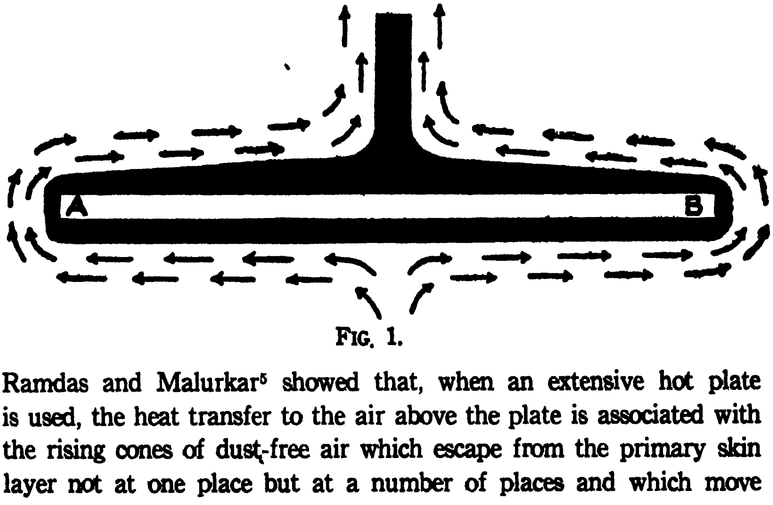

FIG. 1.

Ramdas and Malurkar[5] showed that, when an extensive hot plate is used, the heat transfer to the air above the plate is associated with the rising cones of dust-free air which escape from the primary skin layer not at one place but at a number of places and which move about in a random manner, (Fig. 2). Below the plate the dark layer is thin and uniform.

FIG. 2.

It is clear from the observations made by the previous workers in this field that the dark layer is a fundamental phenomenon arising from some kind of repulsion which a dust particle experiences when it is very close to a hot surface. Attempts to explain the phenomenon in the past have been unsatisfactory because, in the experiments usually made, convection plays a prominent part and makes the conclusions somewhat indecisive. A fresh investigation of the phenomenon was therefore made under special conditions whereby the effect of progressively eliminating the convection below a hot surface could be studied. Mr. M. K. Paranjpe working at the Meteorological Office, Poona, succeeded in completing this investigation. A brief account of the work[6,7] is given below.

1. *Dark space in relation to convection near it.*

A vertical section of the apparatus used is shown in Fig. 3. ABCD is a rectangular metallic vessel (5 cm. by 5 cm.) fitting into a glass cell EFGH, containing a layer of mercury KL which is used as the lower boundary of the confined air cell BC KL. The thickness of the air cell is varied by lowering or raising the level KL. The upper surface BC is heated by pouring hot water into the upper vessel. When cigarette smoke is admitted into the space between BC and KL and a parallel beam of light is passed through a narrow slit at BK towards CL, the phenomena in the air cell become actually visible and may be photographed. In the experiments referred to below the upper hot surface was maintained at 75°C and the cold surface at 30°C.

(*a*) Thickness of the air cell = 2·29 cm.

The vertical section of the convection pattern is shown in Fig. 1 of plate I. There is a thin dark layer just below the hot surface. The space below is occupied by a pair of vortices, the motion being clockwise in the vortex on the right and anticlockwise in the one on the left. At the centre the air is seen to be rising towards the hot surface. The convection in the two vortices tends to throw out a particle towards the hot surface whereas the repelling effect of the hot surface acts in the opposite direction. The thickness of the dark space is only about 0·5 mm.

(*b*) Thickness of the air cell = 0·85 cm.

On decreasing the thickness of the air cell to 0·85 cm. the two vortices decrease in size, separate and move towards the sides of the cell, (Fig. 2, plate 1). The air in the middle of the cell is free from any convectional movements and here the repelling effect of the hot surface on the smoke particles has its full sway. The maximum width of the dark space is as much as 4 mm. at the centre.

(*c*) Thickness of the air cell = 0·54 cm.

A further reduction of the thickness brings about a rapid contraction of the vortices which now become very sluggish. The appearance of the pattern is shown in Fig. 3, plate 1. The dark region now occupies the whole space between the plates, the smoke being driven towards the cold surface everywhere except at the two ends where also, above the vortices, the dark space has widened still further.

(*d*) Thickness of the air cell = 0·34 cm.

Fig. 4, plate 1, shows the pattern; smoke particles are absent everywhere except at the two ends where the last remnants of the two original vortices are just visible.

(*e*) Thickness of the air cell = 0·22 cm.

Lastly Fig. 5, plate 1, shows that at this distance between the two surfaces the smoke particles are driven away towards the cold surface as soon as they are introduced.

It is clear, therefore, that when the convection is quenched by bringing the two surfaces sufficiently near to each other, the repulsion of a particle away from the hot surface has its full sway.

2. *Effect of changing the distance between the hot and the cold surfaces on the repulsion of the smoke layer.*

In this series of experiments the temperature of the upper surface BC (vide Fig. 3), is maintained at 70°C while the lower surface

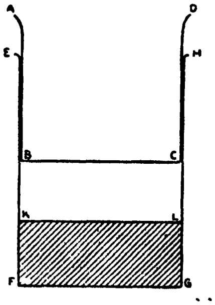

FIG. 3.

is at 30°C. The air in the interspace is kept free from smoke to start with. A puff of smoke is then introduced gently through a narrow metal tube soldered to a small hole at the centre of BC. The puff of smoke does not show any trace of convection or sidewise movement if the thickness of the air cell is less than 5 mm. It is seen to undergo a rapid vertical movement downwards towards the cold surface BC, the upper boundary of the cloud being quite sharp

PLATE I.

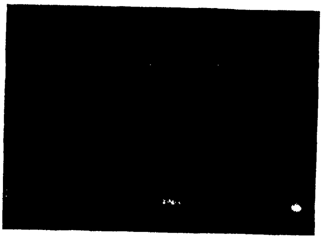

FIG 1.

FIG. 2.

FIG. 3.

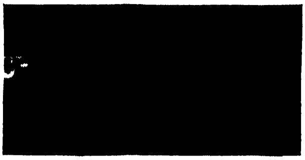

FIG. 4.

FIG. 5.

and horizontal. In the course of a few seconds all the smoke is repelled towards the cold surface and deposited on it. The speed of the downward movement is seen to depend upon the distance between the two surfaces. Actual measurements of the distance from the hot plate traversed by the upper boundary of the smoke at increasing intervals of time and for different thickness of the air cell were made. The values of the velocity of the smoke layer at different distances away from the hot place as obtained from these measurements are given in Table I below :

TABLE I.

Distance between hot surface BC and cold surface KL in cm.	Distance of smoke layer from the hot surface in cm.	Velocity of the smoke layer in cm./sec.
0·90	0·05	0·0083
	0·15	0·0034
	0·24	0·0000
0·60	0·05	0·0182
	0·15	0·0143
	0·25	0·0111
	0·35	0·0054
	0·46	0·0000
0·35	0·05	0·0226
	0·15	0·0226
	0·25	0·0226
	0·35	0·0226

The falling away of the velocity as the particles move away from the hot surface when the thickness of the air cell is 0·6 cm. or more shows that the opposing influence of the convection is felt in these cases. When the thickness of the air cell is 0·35 cm. or less the particles move with a uniform velocity throughout their passage from the hot to the cold surface. In this case convection is totally absent as we have already seen.*

3. *Effect of changing the temperature gradient, while keeping the thickness of the air cell constant at 0·35 cm.*

The rate of movement of the smoke layer was measured when the temperature difference between the hot and the cold surfaces were adjusted to be 46°C, 28°C and 14·5°C respectively. The above temperature differences correspond to gradients of 131°C, 80°C, 41°C per cm. respectively and the corresponding uniform velocities of the smoke layer were found to be 0·0226, 0·0119 and 0·0083 cm. per sec., respectively. For unit temperature gradient, i.e., 1°C per cm. the velocity is therefore $1{\cdot}756 \times 10^{-4}$ cm. per second.

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* Measurements of air temperature made with the help of an interferometer (Vide Ref. 7 above) show that the temperature gradient is also uniform for distances of separation <·35 cm.

Using Stokes' law and considering that the limiting velocity is proportional to the impressed force it is found that the force of repulsion F which a temperature gradient of 131°C per cm. causes on a particle is given by $F = {}^4/_3\, \pi\, r^3\, \rho\, g \times 10{\cdot}71$, where r is the radius and ρ the density of the particle and g is the acceleration due to gravity.

The excess pressure $\triangle P$ exerted by the particle on account of this extra force is of the order of 0·81 dyne/cm.².

Further experiments with single particles moving in a thermal field are in progress. The explanation of the phenomenon from the view point of the Kinetic theory of gases has also been worked out. This will be discussed elsewhere.

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'BEAM' AMPLIFIER

By

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In the course of some high frequency and supersonic frequency work that is being done in this laboratory the following arrangement for an amplifier came to be utilized and as it appears, that this circuit is not so well known, it is thought worth while to describe it in details. The circuit offers, as will be seen, certain advantages over the usual D. C. and A. F. amplifiers.

It is called a Beam-amplifier because it uses the so-called Beam amplifier tube 6 L 6. This is described as a 'new tube', that 'makes use of fundamentally new principles involving the production of beams of high electron density. Two principal results are that the screen does not absorb appreciable power and efficient suppressor action is supplied by space charge effects between screen and plate.'

Ordinary direct current amplifiers have their own disadvantages. In the usual arrangement each stage requires independent Grid-bias battery and those bias-voltages go on increasing with each succeeding stage. The voltages are also critical and whether dry cells or accumulators are used, the set-up becomes a clumsy one. If automatic or self-bias is used the amplification per stage is sacrificed. The Loftin-white arrangement of direct coupling suffers similarly from a severe handicap.

What is the fundamental source of all these troubles? The ordinary control grid of a triode valve cannot be directly joined to points of high positive potentials with respect to its cathode without introducing saturation. If however the grid can be made positive without producing saturation and if the grid-current is negligible the problem admits of a solution.

The Beam amplifier valve 6 L 6 seemed to satisfy these conditions in the following manner. The ordinary control grid is used as a regulator of emission from the cathode and as this grid always remains at some fixed negative potential it may be regarded as a 'virtual cathode.' The screen-grid of the valve itself is used as a control grid for the plate current. Then the *Independent* characteristic of the valve 6 L 6 is as follows. Table No. 1, Fig. No. 1.

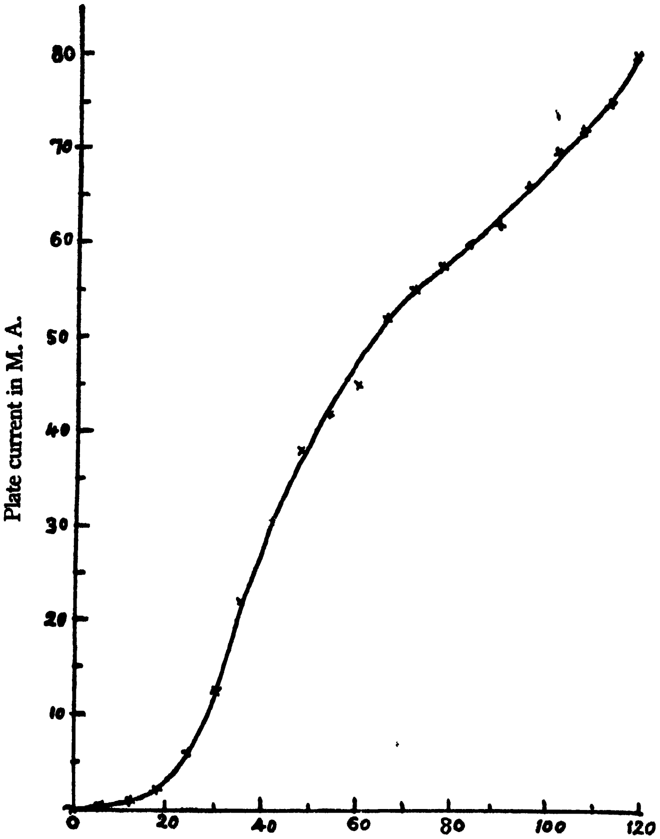
TABLE I.

6 L 6 valve secondary Independent Characteristic

(*Screen Grid Volts—Plate current characteristic*)

Plate voltage = 200.

Vg Screen volts	(Plate current in mA)
0	0
6	·3
12	·1
18	2·3
24	6
30	12·5
36	22
48	38
54	42
60	45
66	52
72	55
78	57·5
84	60
90	62
96	66·5
102	70
108	72
114	75
120	76



Screen Grid voltage.
FIG. 1.

It is of course obvious that a certain screen current is flowing through the circuit C S P N.

If now such a valve is joined as shown in Fig. 2 the screen current will flow through the plate-resistance of the preceding valve and will produce a voltage drop across the resistance and will effectively lower the potential of point P (Fig. 2). When this is taken in consideration we get what we call the *Interdependent* characteristic of the valve. Let us suppose that R is the optimum resistance of coupling and I is the *total change of current* flowing through R (made up of i_1 the change in the plate current flowing through R together with i_2 the change in the screen-current of the succeeding valve,) flowing due to voltage change V of the screen grid used as a signal. Then unless the ratio $\frac{IR}{V}$ is greater than unity the valve will fail to work as an amplifier. Thus the valve must have *Interdependent secondary* amplification factor greater than unity. This shows why ordinary screen-grid or pentode valves cannot generally be used for this type of arrangement and forms an interesting speciality of 6 L 6.

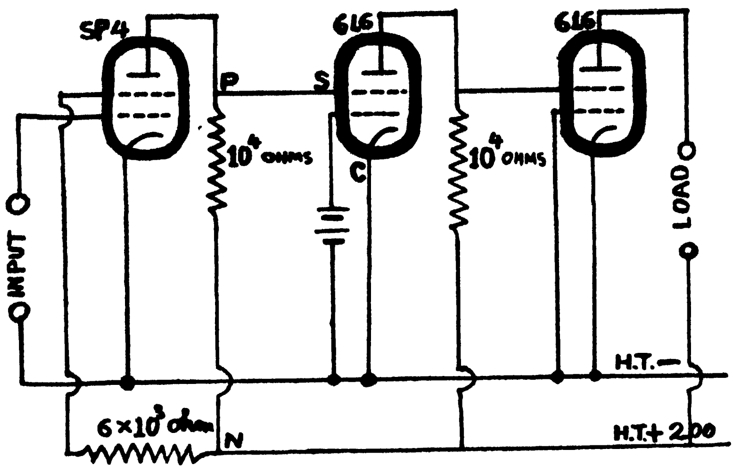
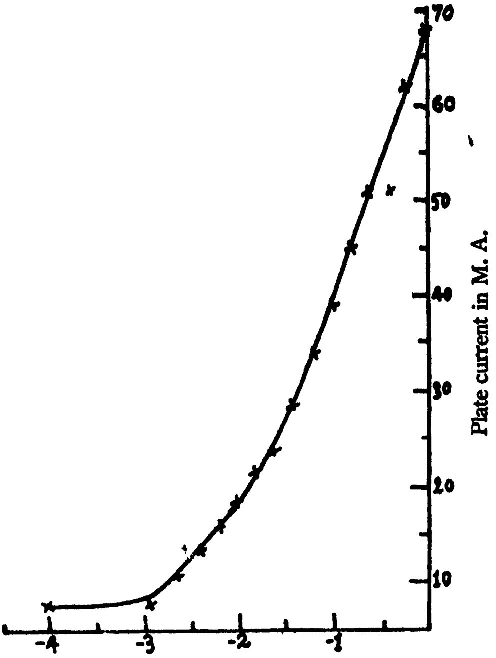


FIG. 2.

TABLE II.

Resultant characteristic of the amplifier.

Vg (Grid volts) negative.	I (plate current)
0	68 m. a
·2	62
·4	51
·6	51
·8	45
1	39
1·2	34
1·4	28·5
1·6	24
1·8	21·5
2	18·5
2·2	16
[illegible]	13·5
[illegible]	11
[illegible]	7·6
[illegible]	7·6

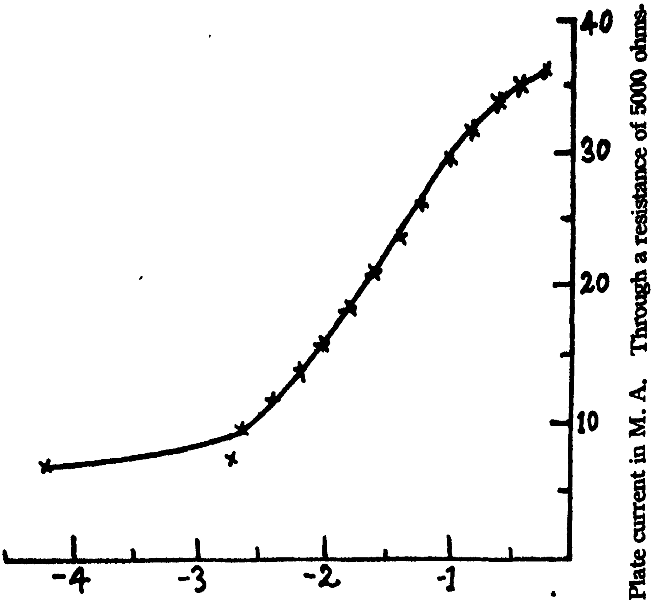


Grid volts.
FIG. 3.

For the first stage Mullard S P 4 is used the 2nd and 3rd stages are built around 6 L 6, and the over-all characteristic of the amplifier is shown in (Table II Fig. 3).

TABLE II.
Out-put Resistance—(5000)
Plate voltage (200 volts)

Vg (Grid volts) negative.	I. (Plate current in M. A.)
0	36
·2	36
·4	35·5
·6	34·4
·8	32·2
1	29·8
1·2	26·5
1·4	24
1·6	21·4
1·8	18·8
2	16
2·2	14
2·4	12
2·6	10
2·7	7·4
4·2	7·2



Grid volts.

FIG. 4.

One noteworthy feature of the arrangement is that it contains but 3 valves and 2 resistances only ; it is therefore extremely compact and as it is only a resistance coupled (not resistance capacity coupled) arrangement, there is no reason why it should not be useful for D.C. A.F. and also for R.F. amplification. It is giving us very good service from 0 to 20 K.C. and it is intended to test it for still higher frequencies as soon as standard H. F. resistances are available. At very high frequencies the inter-electrode capacities will naturally have their effect.

Apart from the actual use to which it can be put and the limitations it may have at present, the writer likes to think of it as a forerunner of a universal amplifier. The modern trend in the design of vacuum tubes makes one hopeful of such an arrangement and the progress that one sees in the design of valves such as 6 L 6 or deflection type of valves may culminate in novel ways in which amplifiers can be built from such an ordinary beginning.

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THE STUDY OF THE OXY-COALGAS FLAME BY BAND SPECTRA

By

N. R. TAWDE & J. M. PATEL

Royal Institute of Science, Bombay.

1. INTRODUCTION.
2. THE PROBLEM.
3. EXPERIMENTAL.
4. RESULTS & OBSERVATIONS.
    - (*i*) Intensities.
    - (*ii*) Transition probabilities.
    - (*iii*) Comparison with theoretical values.
    - (*iv*) Vibrational Energy & Temperatures.
    - (*v*) Intensity Centres.
5. CONCLUSIONS & DISCUSSION.

I. INTRODUCTION.

It is a common observation that a bunsen burner supplied with coal gas when lighted gives a luminous flame, gold-yellow in colour, if the air supply is completely stopped. If the air is gradually admitted by opening the air cap, the extent of the flame gradually diminishes, at the same time, the luminosity of the flame changes from gold-yellow to colourless. A cone is seen in the flame after some time which diminishes with the increase of air supply. The colour of the cone changes and becomes distinct greenish-blue when the air supply is maximum. Thorpe[1] states that as the colour of the flame changes from gold-yellow to non-luminious, the temperature as well as the volume of the flame change, the volume being the least when the temperature is the highest.

METHODS OF PRODUCING THE FLAME.

Thorpe[1] thus describes three different ways of producing the flames.

(1) By igniting the inflammable mixture as it issues into a neutral atmosphere.

(2) By allowing one of the combining gases to issue from an orifice into an atmosphere of the other,

(3) By having one gas in excess in the mixture and to allow it to issue into an atmosphere containing the other.

Different conditions exist in all these three methods. The variation of the gases causes the variation in the blue cone, as well as in the temperature of the flame. The velocity of the gas tends the inner cone to decrease, i.e., the velocity of the cone is opposite to that of the gas. From such observations Thorpe[1] remarks, "speaking of each flame as a whole, we may say that the hotness is greater in proportion as the surface is less." It is interesting to verify this statement by a number of experiments.

METHODS OF MEASURING THE TEMPERATURE

Different authors used various methods to measure the temperatures of flames. They are summarised as follows :—

(1) By using wires of different melting points.

(2) By exploding the gaseous mixtures and calculating the temperature from the consequent increase of pressure.

(3) By means of thermocouples.

(4) By the use of the optical pyrometer in cases, where the flame contains incandescent solids (the line reversal method).

(5) By analysis of interconal gases and the application of thermodynamics.

(6) By measurement of spectral intensities in a flame.

Of these, methods (1) and (2) give results of only rough approximations. Consequently they have been rarely used. Methods (3) and (4) have been used by a number of investigators who have found the temperatures of different flame sources. The pyrometer method is the simpler of the two as far as the experimental technique is concerned. But the results derived from it are not expected to be so accurate as in the case of the thermocouple method. It is used in industrial concerns for rapid estimations of temperatures. The estimations and calculations involved in method (5) are laborious. Hence it is not much in use. But the last one i.e., (6) is relatively of recent origin and is in the process of development. It has so far been used by some investigators to determine the effective temperatures of flames and other sources in which characteristic band spectra are emitted.

THE PROBLEM

In view of the theoretical importance which the subject of spectral intensities has received, it seems worthwhile to study experimentally a few of the aspects of intensities connected with electronic band spectra of diatomic molecules. These have come to the forefront on account of visual estimates of intensities on which all our theoretical calculations were based and more so on account of some divergent conclusions reached by different authors from the accurate quantitative data that is already at our disposal.

No serious attempts were made for a long time to make quantitative measurements of intensities in band systems, probably on account of the difficulties involved in the work due to large spectral ranges. It was Elliot[2] who touched the subject for the first time and made his measurements of intensities on β—system of BO. This work was followed by that of Ornstein and Brinkman[3] on violet CN-system. Among the recent workers in the field, we have Johnson and Tawde,[4] Tawde[5, 11] and Wurm.[6] The results of all these authors when examined critically reveal points of unusual character which cannot be settled unless experimental material is in our possession. In the following pages we shall describe experiments undertaken to investigate the C_2 (Swan) system. The gross intensities in the system have been thoroughly estimated by Johnson and Tawde[4] by the methods of spectral photometry. The bands of the system have been produced by those authors under five different conditions of excitation and the results have shown certain features which require further elucidation from experiments. This is specially so with the effective temperatures of sources derived on the assumption of vibrational distribution of energy, which in many cases do not coincide with true temperatures.

It was, therefore, thought desirable to examine this point further in the case of oxy-coal gas flame in which these bands occur without dilution. The fact that swan bands are due to C_2 molecule is to be ascribed to the formation of C_2 from coal gas and oxygen at a certain stage during the process of combustion in the flame. The high or low temperatures resulting from combustion of two gases in certain proportions is a consequence of the distribution of energy among the vibrational and rotational levels and hence the intensity distribution among bands of the system and in the fine structure.

By applying, therefore, the band spectroscopic methods, especially the intensity measurements, it seemed worthwhile to study by vibrational distribution, the combustion and hence the temperature within the oxy-coal gas flame as these results along with similar ones of previous authors but by other methods, would offer us some points of comparison. The advantage in selecting the swan system is that it occurs wholly within the visible region and the bands comprising it do not run quite close to each other in sequences, an advantage in intensity measurements. Its distribution, moreover, has been characterised as of normal type. The two flame gases, viz., oxygen and coal-gas could be passed at different pressures and allowed thus to mix within the jet in different proportions.

3. EXPERIMENTAL.

A specially prepared blow-pipe burner with a jet opening of 1·95 mms. was used in these experiments to produce the flame. The gases (coal-gas and oxygen) were allowed to enter the blow-pipe through the proper inlets. The gas pressures were measured by means of two oil manometers. Mercury manometers were tried in the beginning, but due to high density of mercury, they did not give accurate results and were given up. The coal-gas pressure was always kept constant i.e., 4 cms. and the oxygen pressure was varied from 3·2 cms. to 0·8 cm., thus getting the required gas/oxygen ratios to be 1·25, 2, 3, 4, 5. The oxygen gas was of a commercial type-supplied in cylinders by the Lightfoot Refrigeration Co. The coal-gas supply was from usual gas fittings of the laboratory. Its pressure was found to be slightly fluctuating, but it was kept constant by keeping the oil level steady in the manometer by means of a pinch-cock between the gas tap and the blow-pipe. The oxygen pressure in the burner was constant throughout the experiment as the gas was coming from the cylinder at a fairly constant pressure of about 80 atmospheres.

As has been shown earlier, in a work of this type, a low dispersion spectrographic instrument was found necessary and hence a Hilger constant deviation glass prism spectrograph was used. Its dispersion varied from 18·4 A. U. per mm. at 4365 Å to 76·6 A. U. per mm. at 6191 Å.

Two exposures were given on the plate one after the other, one for spectrum to be measured and another for the intensity marks. The procedure followed was to photograph the spectrum for an interval, sufficient to cause a measureable blackening on the plate. The regular slit was then removed and replaced by the step-slit. The exposure was given through this to the standard lamp for an interval of time equivalent to that of the spectrum so that the intensity marks came immediately after the spectrum on the plate. The importance of the equality between the times of exposure for the spectrum and for the comparison intensity marks has been pointed out by Rekveld.[7] In adjusting the time of exposure it is essential that the spectrum blackening should be intermediate between the maximum and minimum of the intensity marks. This was determined after several trials. The standard lamp used was supplied by General Electric Company, Wembley, calibrated by Johnson and Tawde at Government Chemical Laboratory, London, and obtained by us through their courtesy.

It must be remembered that in the system under investigation, there are bands ranging from maximum to minimum intensity. Consequently, it was not possible to get the whole system photographed at a time with the exposures of the order needed for satisfying the above conditions: A small group of five or six bands of nearly equal intensity was chosen at a time and exposure given to it. Then a next group of similar number was taken including 2 or 3 bands of the first group which were, of course, intermediate in intensity between the first and the second group. It was thus necessary to divide this system of twenty-two bands into convenient groups in order to arrive at the estimation of their intensities on one relative scale. Several exposures were, therefore, found to be essential to get the intensity values of all the bands. The common bands between several groups enabled to correlate one exposure with the other and thus eliminated many errors involved in the photographic technique. In satisfying all the above conditions it was found that for each ratio of the coal-gas oxygen pressure, about four exposures gave the intensity distribution in the whole system.

Many practical difficulties had to be encountered in adjusting the equality of the time of exposures. Either the standard light source was too strong in comparison to the flame or vice versa. These were solved as far as possible by adjusting the relative distances of the sources from the spectrograph slit, so as to get blackening of the comparative order. It was, however, kept in mind that the sources were not too near the slit as to cause non-uniformity of light falling on it. Where either of the sources was too strong in intensity even at longer distances, a device for cutting down the intensities to the requisite degree by neutral filters was adopted, and this procedure was found to be very effective.

The standard lamp during the exposure time was strictly run at 12 volts with a current of 1·9 amps. in its filament, these being the conditions governing its calibration. No lens was used in front of this source, thus allowing the uniform distributon of light over the slit.

The photographic plates were the Ilford Rapid Process Panchromatic and were backed. These being of large grain, require less time of exposure which is advisable in work of this type. They were, moreover, found to give a good contrast. The development was carried out under uniform conditions. A swirling device was used in order to cause the uniform flow of the developing solution over the plate. The temperature of all the photographic reagents used was maintained strictly constant at 18°C throughout, as also the time of developing the plate. The plates were developed in complete darkness immediately after the exposure. The developing solution was rodinol diluted in the ratio of 1 to 18 parts of water.

MICROPHOTOMETRY

The final plates chosen for measuring were microphotometered by means of a self-recording instrument. This was a Zeiss microphotometer belonging to the Science College, Patna, where this part of the work was done by the courtesy of the authorities.

Before proceeding to obtain a microphotometer record, the spectrophotometer was tested for accuracy and consistency. For this, the spot of light which scans the plate was reduced to a size much smaller than the width of the band, satisfying at the same time the condition that it is able to cause maximum deflection between the limits of the transparency of the background of the plate and the perfect opacity. This was tested every time a new plate was mounted on the carriage of the microphotometer. To test the consistency and the reproducing power of the microphotometer, a trial record was taken in the case of a few band-heads by running the plate in one direction and then in the opposite. When this record did not show any duplicity of the curve obtained, the microphotometer was taken to be in a perfect adjustment.

The procedure of measuring the plates under the microphotometer can be easily explained as follows :—The plate is adjusted on the carriage of the microphotometer so as to get the spot of light to cross the required bands. This would give a photographic record of the measure of blackening due to the band heads. When this has been obtained, the plate is removed and again mounted in such a way that the spot of light could run along the line of wave-length of one of the band heads to be measured so as to cross the intensity marks. If λ is the wave-length, then the subsidiary spectrum taken on the other side of the intensity marks would enable to define exactly the direction of movement across the intensity marks. Thus we get two types of records for each band head, one for its own blackening and the other for the calibrated intensity marks opposite to its wave-length. In this way, several microphotometer records were obtained for each of the coal gas/oxygen ratio readings.

Measurements were made on the records for i_0 and i values from which we could express the densities of blackenings due to intensity marks in each wave-length of band to be measured and a graph prepared expressing the $\log \frac{i^o}{i}$ values against the widths of the step-slit. These latter are obviously taken to be proportional to intensities. The scale is such that the maximum slit-width represents an intensity of 100 units. These widths were measured accurately by microscope. After blackening-intensity curves are prepared for the given bands on any one plate, the actual blackenings due to the peaks are located on these and expressed in terms of intensities. The comparison between different plates was obtained by a few bands kept common in both. Thus if a, b, c and d, e, f are the two sets of band heads measured on one plate and d, e, f and g, h, j are those on the other, then the intensity scale for each of the sets of six bands differs according to the constant of the plate. The ratio between the scale of the common bands d, e, f on each enables intensities for all the bands a, b, c ; d, e, f ; g, h, j to be placed on one common scale. We thus get all the bands on a relative scale of intensity which takes into account the variation of plate sensitivity with wave-length. To express this scale in terms of the energy units of the standard lamp, we multiply these values with the energy units of the lamp at corresponding wave-lengths by the help of its calibration curve. These values are then expressed on a scale. No correction is necessary for the reflection and absorption losses within the spectrograph as these are expected to be the same both for the spectrum and the accompanying intensity marks.

4— Results and Observations.

(i) *Intensities and* I/ν^4 *values.*

A relative scale of intensities has been fixed which is based on the assumption that the (o, o) band has the intensity of 100 units. All the other bands are expressed in terms of this. For all the five ratios, the intensities determined are given in Table I.

Table I.

I and I/ν^4 values.

Bands.	COAL GAS/OXYGEN RATIO.				
	1·25	2·0	3	4	5
2,0	14·9 *5·48*	8·43 *3·09*	18·0 *6·60*	14·6 *5·38*	7·48 *2·74*
3,1	22·4 *8·13*	27·3 *9·93*	38·8 *14·1*	29·0 *10·5*	19·4 *7·06*
4,2	24·5 *8·84*	49·2 *17·8*	57·7 *20·8*	43·6 *15·7*	23·9 *8·64*
1,0	61·6 *30·9*	54·0 *27·1*	66·6 *33·4*	62·9 *31·5*	70·2 *35·1*
2,1	32·6 *16·0*	34·3 *17·0*	40·8 *20·1*	50·2 *24·7*	48·1 *23·7*
3,2	27·8 *13·5*	31·2 *15·1*	35·4 *17·2*	47·9 *23·2*	40·6 *19·7*
4,3	17·0 *8·17*	18·5 *8·86*	23·1 *11·1*	31·5 *15·1*	28·4 *13·6*
5,4	23·1 *10·9*	26·4 *12·5*	28·5 *13·5*	39·4 *18·7*	33·6 *15·2*

TABLE I (*Continued*)

Bands.	COAL GAS/OXYGEN RATIO.				
	1·25	2·0	3	4	5
0,0	100·0	100·0	100·0	100·0	100·0
	71·0	*71·0*	*71·0*	*71·0*	*71·0*
1,1	28·3	35·9	37·9	43·5	41·0
	19·5	*24·8*	*26·1*	*30·0*	*28·3*
2,2	8·3	10·8	11·1	10·9	10·2
	5·61	*7·27*	*7·47*	*7·32*	*6·86*
0,1	24·9	29·5	35·2	40·1	35·7
	25·1	*29·8*	*35·5*	*40·4*	*35·9*
1,2	18·2	14·1	25·2	28·3	22·4
	18·3	*14·2*	*24·4*	*28·5*	*22·6*
2,3	13·1	8·15	17·1	20·4	13·7
	13·2	*8·20*	*17·2*	*20·5*	*13·8*
3,4	8·32	5·28	11·9	13·4	9·97
	8·37	*5·31*	*12·0*	*13·4*	*10·0*
4,5	4·36	4·13	4·63	6·6	4·69
	4·38	*4·17*	*4·65*	*6·7*	*4·71*
0,2	5·16	9·09	6·83	10·1	12·7
	7·58	*13·2*	*10·0*	*14·9*	*18·6*
1,3	5·29	9·92	6·13	7·74	10·7
	7·41	*13·9*	*8·60*	*10·8*	*15·0*
2,4	3·98	8·89	5·03	6·26	8·55
	5·36	*12·0*	*6·78*	*8·43*	*11·5*
3,5	2·77	4·68	4·45	6·10	7·56
	3·59	*6·07*	*5·77*	*7·91*	*9·80*
4,6	2·43	3·16	4·12	4·51	4·93
	3·05	*3·97*	*5·18*	*5·66*	*6·19*
5,7	1·63	2·40	1·91	3·25	2·64
	1·99	*2·93*	*2·33*	*3·79*	*3·22*

The numbers in *Italics* indicate I/ν4 values.

The importance of the quantity I/ν4 arises on account of the fact that I the intensity of any band is proportional to the 4th power of the frequency emitted, the transition probability and the exponential due to Boltzmann distribution of vibrational energy in the initial state at any temperature T. Thus

$$I = A.\ \nu^4.\ P_{v'v''} e^{-\frac{E_{v'}}{kT}} \quad \ldots\ldots\ldots\ldots \quad (1)$$

where A = constant

$E_{v'}$ = Initial vibrational energy

$P_{v'v''}$ = Transition probability from initial level v′ to final level v″.

k = Boltzmann Constant.

T = Absolute temperature.

Therefore,

$$I/\nu^4 = A.P_{v'v''}e^{-\frac{E_{v'}}{kT}} \quad . \; . \; . \; . \; , \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The quantity on the left hand side is proportional to the statistical weight of the band concerned. The values of I/ν^4 are therfore calculated for each band and entered in Table I, below the values of intensities. The weights $\Sigma|/\nu^4$ for each initial vibrational level derived from I/ν^4 values are entered in Table II.

TABLE II.

$I/\nu4$ values of initial levels.

Initial vibration level.	COAL GAS/OXYGEN RATIO.				
	1·25	2	3	4	5
$v'=0$	103	114	116	126	125
$v'=1$	76·2	80·0	92·6	101	101
$v'=2$	45·7	47·4	58·2	66·4	58·6
$v'=3$	33·6	36·4	49·0	55·1	46·6
$v'=4$	24·4	34·7	41·7	43·2	33·1
$v'=5$	12·9	15·4	15·8	22·5	19·1
Weight of the system.	295·8	327·9	373·3	414·2	383·4

(ii) *Transition Probabilities*

The equation (2) above can be written in the form

$$I/\nu^4 = N.\,P_{v'v''}e^{-\frac{E_{v'}}{kT}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; , \; . \; . \; . \quad (3)$$

$$= \Sigma\, I/\nu^4\, P_{v'v''}e^{-\frac{E_{v'}}{kT}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

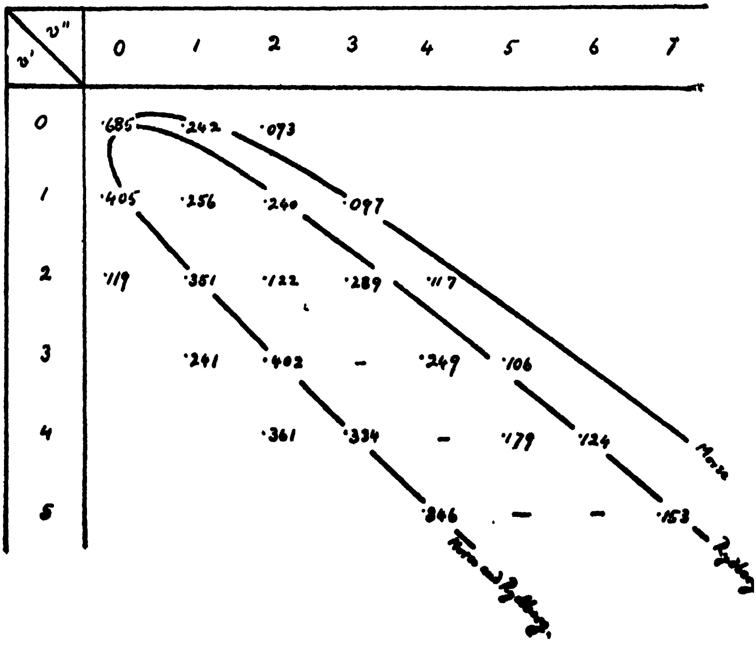
where N represents the number of molecules in the initial state and is replaced by $\Sigma I/\nu^4$ the satistical weight of that level in equation (4).

Therefore,

$$\frac{I/\nu^4}{\Sigma I/\nu^4} \infty P_{v'v''} e^{-\frac{E_{v'}}{kT}} \quad \ldots\ldots\ldots\ldots \quad (5)$$

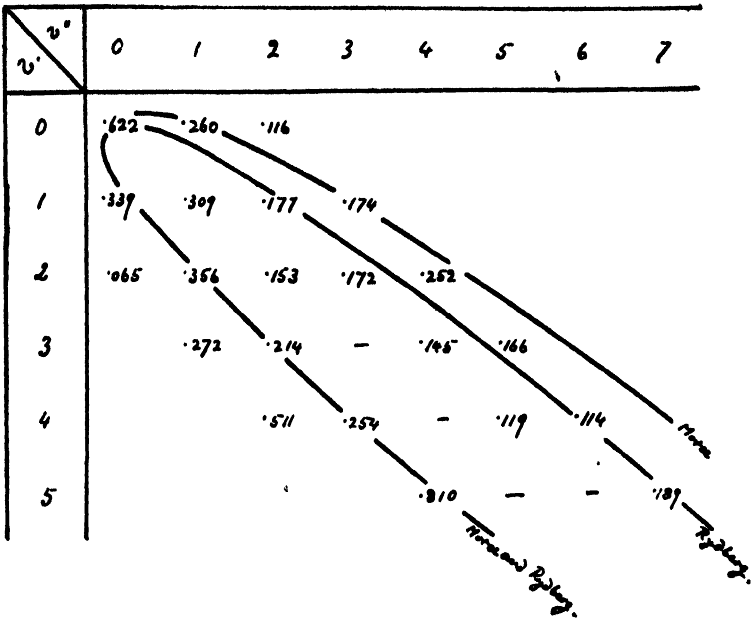
The ratio on the left side in the above relation represents a number proportional to the relative transition probability of any band. To calculate this, we have divided I/ν^4 value of each band by the appropriate $\Sigma I/\nu^4$ for each v′-level and thus arrived at the values in Figs. 1, 2, 3, 4, 5. They represent the experimental values of transition probabilities.

FIG. 1.—Transition Probabilities Gas/Oxygen Ratio = 1·25.



v′ \ v″	0	1	2	3	4	5	6	7
0	·685	·242	·073					
1	·405	·256	·240	·097				
2	·119	·351	·122	·289	·117			
3		·241	·402	–	·249	·106		
4			·361	·334	–	·179	·124	
5					·346	–	–	·153

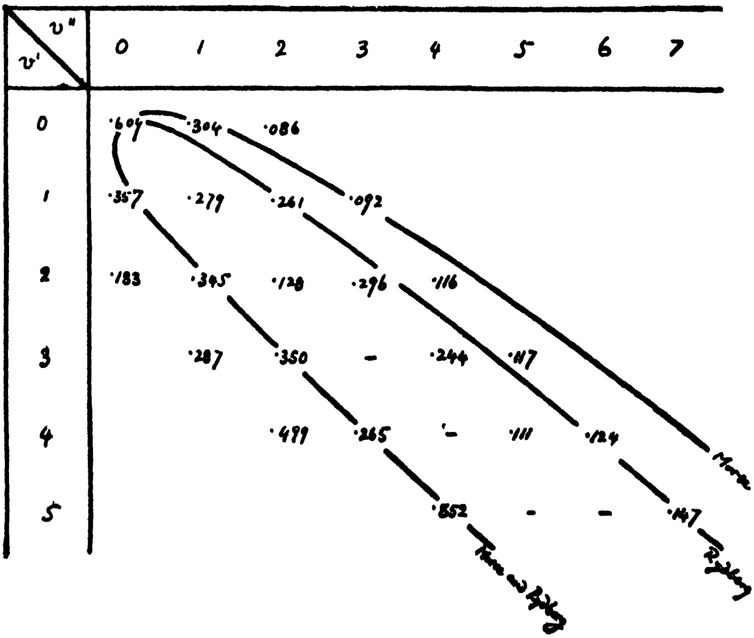
FIG. 2.—Transition Probabilities Gas/Oxygen Ratio = 2.



v' \ v''	0	1	2	3	4	5	6	7
0	·622	·260	·116					
1	·339	·309	·177	·174				
2	·065	·356	·153	·172	·252			
3		·272	·214	–	·145	·166		
4			·511	·254	–	·119	·114	
5					·810	–	–	·189

Morse
Rydberg.
Morse and Rydberg.

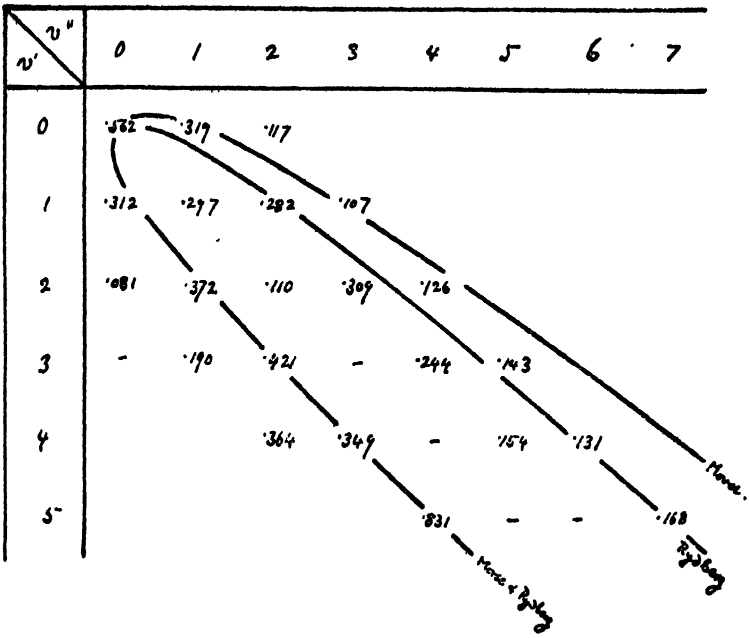
FIG. 3.—Transition Probabilities Gas/Oxygen Ratio = 3.



v' \ v''	0	1	2	3	4	5	6	7
0	·604	·304	·086					
1	·357	·279	·261	·092				
2	·183	·345	·128	·296	·116			
3		·287	·350	–	·244	·117		
4			·499	·265	–	·111	·124	
5					·852	–	–	·147

Morse
Rydberg
Morse and Rydberg

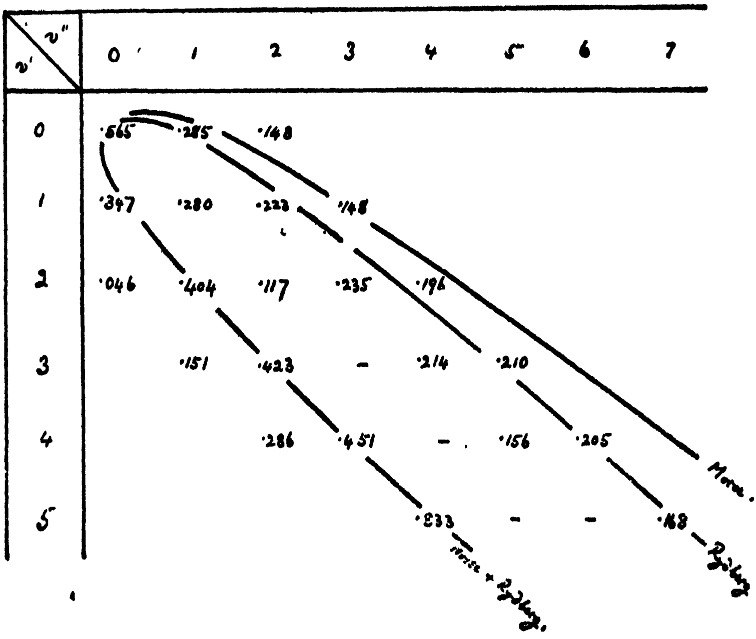
FIG. 4.—Transition Probabilities Gas/Oxygen Ratio = 4.



v' \ v''	0	1	2	3	4	5	6	7
0	·582	·319	·117					
1	·312	·277	·282	·107				
2	·081	·372	·110	·309	·126			
3	-	·190	·421	-	·244	·143		
4			·364	·349	-	·154	·131	
5					·831	-	-	·168

Morse.
Rydberg
Morse & Rydberg

FIG. 5.—Transition Probabilities Gas/Oxygen Ratio = 5.



v' \ v''	0	1	2	3	4	5	6	7
0	·565	·285	·148					
1	·347	·280	·223	·148				
2	·046	·404	·117	·235	·196			
3		·151	·423	-	·214	·210		
4			·286	·451	-	·156	·205	
5					·233	-	-	·168

Morse.
Rydberg
Morse & Rydberg.

(iii) *Derivation of theoretical results and their comparison with experimental values.*

(*a*) Morse's potential energy expression.

According to the graphical method of Condon, we have arrived at the values of maximum transition probabilities by drawing the potential energy curves accurately to scale by means of the expression of Morse[8] given below :

$$U\ (r) = D_e \left(1 - e^{-ax}\right)^2$$

The spectroscopic constants in this expression for C_2 molecule (Swan System) are taken as those given in a previous paper by Johnson and Tawde.[4] The theoretical locus of maximum transition probabilities is indicated by parabolas in Figs. 1, 2, 3, 4, 5.

(*b*) Rydberg's potential energy function.

We have also shown in the same figures, the locus of maximum transitions by using Rydberg's expression, which though empirical, has been found to give good account of itself. For instance, Johnson and Dunstan[9] in the case of BeO and Tawde[5] in the case of N_2 (second positive) find the results of maximum transitions derived from it agree better with experiment. The form of Rydberg's expression is

$$U\ (r) = D_e\ (ax+1)\ e^{-ax}$$

Except for a, the values of spectroscopic constants in the above expression are the same as those in More's. For *a*, the values for upper and lower states are calculated as

$$a' = 2{\cdot}668 \qquad ; \qquad a'' = 2{\cdot}072$$

(iv) *Vibrational Energy and Temperatures.*

It can be shown from equation (1) that

$$I/\nu^4 = Ae^{\frac{-E_{v'}}{kT}} (P_{v',\,0} + P_{v',\,1} + P_{v',\,2} \ldots\ldots) \quad . \quad . \quad . \quad . \qquad (6)$$

If we assume that $\sum_{v'} P_{v'v''}$ the sum of transition probabilities practically the same for all v″—progressions, we get

$$\Sigma\, I/\nu^4 \propto e^{\frac{-E_{v'}}{kT}} \quad \ldots\ldots\ldots\ldots\ldots \qquad (7)$$

Taking $\Sigma\ I/\nu^4$ to be proportional to N. the number of molecules in the initial vibrational state, the above expression can be written as

$$N = N_0\, e^{\frac{-E_{v'}}{kT}} \quad \ldots\ldots\ldots\ldots\ldots \qquad (8)$$

where N_0 = number of molecules in the zero vibrational state. The above equation (8) can be rewritten as

$$E_{v'} = kT \log \frac{N_0}{N} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; , \qquad (9)$$

Now writing

$$E_{v'} = hc\left[\omega'_e\,(v'+\tfrac{1}{2}) - \omega'_e x'_e\,(v+\tfrac{1}{2})^2\right]$$

we get

$$\omega'_e\,(v'+\tfrac{1}{2}) - \omega'_e x'_e\,(v'+\tfrac{1}{2})^2 = \frac{k}{hc}\;T\;\log_e \frac{N_0}{N} \quad . \; . \; . \qquad (10)$$

Substituting the values of vibrational constants for the upper $B^3\pi$ state of C_2—Swan System, we get

$$1792{\cdot}77(v'+\tfrac{1}{2}) - 19{\cdot}35(v'+\tfrac{1}{2})^2 = 1{\cdot}6083\;T\;\log_{10}\frac{N_0}{N_{v'}} \quad . \qquad (11)$$

Converting from N_0 to $N_{\frac{1}{2}}$ basis, we get

$$1792{\cdot}77\;v' - 19{\cdot}35\;v'(v'+1) = 1{\cdot}6083\;T\;\log_{10}\frac{N_{\frac{1}{2}}}{N_{v'+\frac{1}{2}}} \quad . \qquad (12)$$

The above equation (12) has been derived on the assumption of statistical equilibrium of molecules in the initial vibrational states at a temperature T. This temperature of equilibrium can be calculated if we know the expression on the left hand side and the quantity $\log_{10}\frac{N_{\frac{1}{2}}}{N_{v'+\frac{1}{2}}}$ and will be termed the effective 'vibrational' temperature. By constructing graphs showing $\log_{10}\frac{N_{\frac{1}{2}}}{N_{v'}+\frac{1}{2}}$ as a function of vibrational energy, we could get the slope 1·6083 T and hence the absolute temperature T. These temperatures for all the five gas/oxygen ratios are given below :

Coalgas/oxygen ratios :	1·25	, 2	, 3	, 4	, 5 .
Temperatures :	6200°K,	6600°K,	7800°K,	8200°K,	6900°K.

A curve is drawn connecting the gas/oxygen ratios and the resulting temperatures. This is given in Fig. 6. Another curve is plotted in Fig. 7 showing the relation between the gas/oxygen ratios and the length of cone in the flame as this has a bearing on temperature.

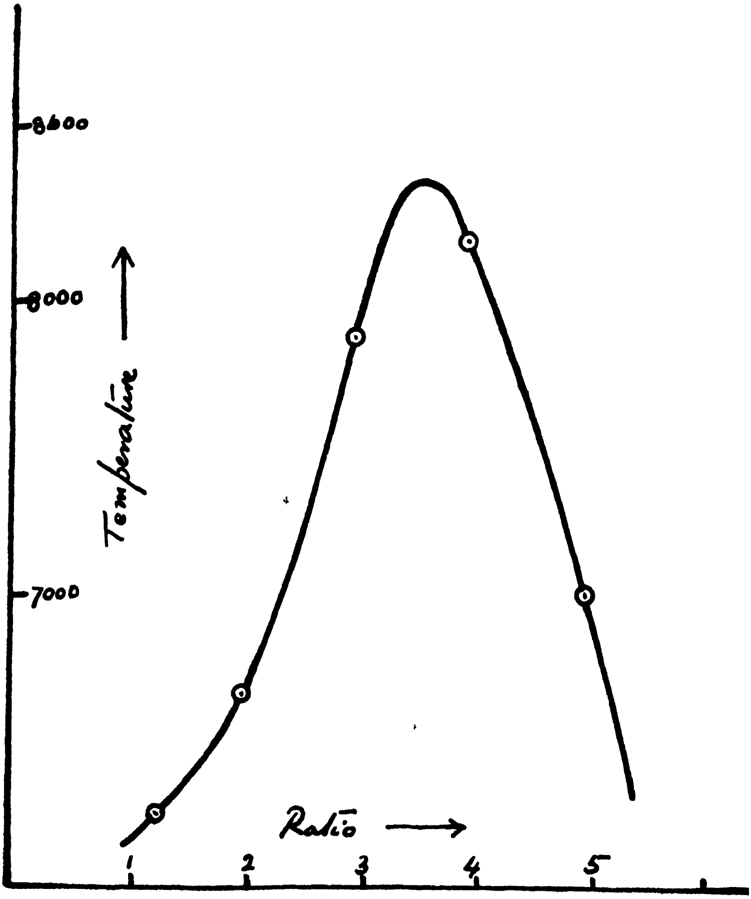


Fig. 6

(v) *Intensity Shifts*

The method of studying the intensity shifts has been given by Johnson and applied by him in the study of N_2 (first positive) system.

If I_1 the intensity at λ_1

I_2 „ „ „ λ_2

I_3 „ „ „ λ_3

and so on ....

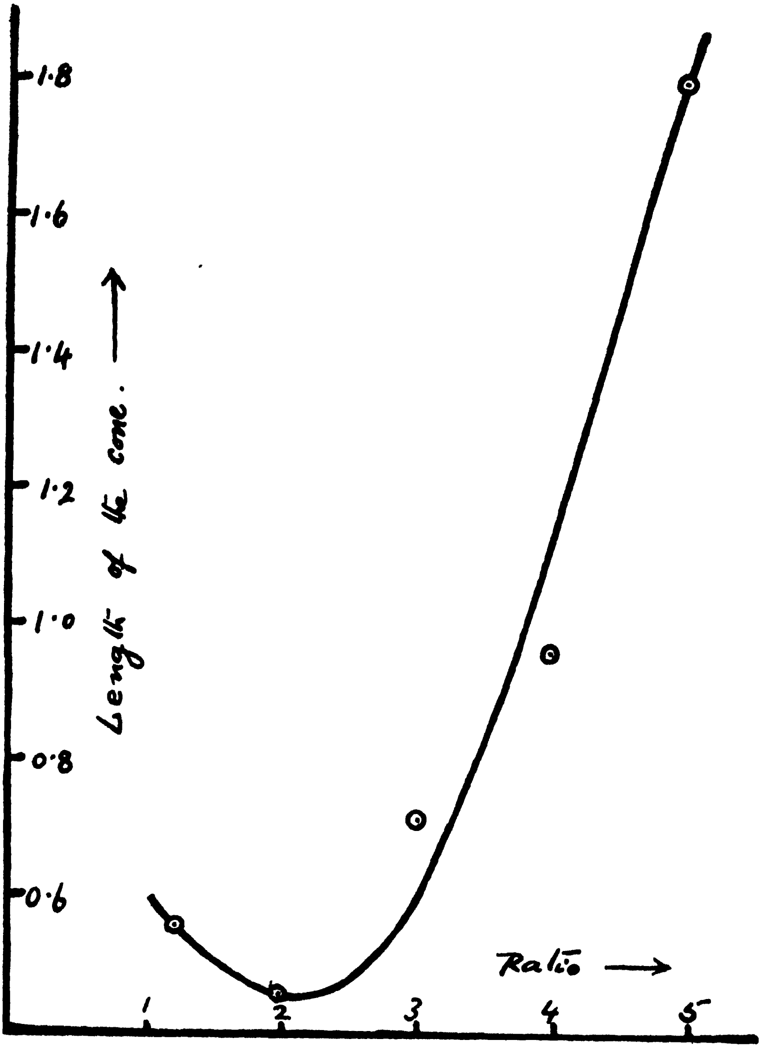


Fig. 7

we can get the centre of intensity for the whole group of wavelengths by the following equation :

$$\bar{\lambda} = \frac{I_1\lambda_1 + I_2\lambda_2 + I_3\lambda_3 \; . \; . \; . \; .}{I_1 + I_2 + I_3 \; . \; . \; . \; .}$$

$$= \frac{\Sigma I \lambda}{\Sigma I}$$

where $\bar{\lambda}$ is expressed as the wavelength at which the 'centre' of intensity lies. By centre of intensity, it is meant as if the centre of gravity of the whole set of intensities or distribution of different intensities in a group.

In a work of this type where there are large groups of intensities, *viz.*, intensities of sequences in a system and those for the whole system under different conditions, a study of $\bar{\lambda}$ values as above would serve a source of useful information. We have therefore calculated these for each of the sequences and for the whole system under all the conditions of the gas/oxygen ratios. These results are entered in Table III.

TABLE III.

Intensity centres for sequences and system.

Sequences.	COAL GAS/OXYGEN RATIOS				
	1·25	2	3	4	5
0,2	6077·9	6084·5	6072·3	6075·0	6082·3
0,1	5577·6	5588·6	5579·8	5578·2	5583·1
0,0	5153·6	5151·4	5151·0	5150·5	5150·9
1,0	4712·0	4709·7	4710·5	4707·1	4709·4
2,0	4371·6	4368·8	4370·0	4370·4	4370·1
Intensity centres for the system.	4996·0	4996·5	4981·3	5008·4	5050·3

5. Conclusions and Discussion

The results of intensities and transition probabilities show good agreement with established relations as regards the fundamental concepts of Condon's theory. The course of maximum transition probabilities remains almost the same in all the five cases of gas/oxygen ratios as can be seen from Figs. 1 to 5. This leads us to conclude that the distribution of transition probabilities is independent of the conditions in the flame. It appears that the process of coal gas-oxygen combustion in the flame takes place pretty slowly so as not to cause any wide departure in the course of the maximum transitions from one condition to the other, except for a new temperature equilibrium which is probably attained as a result of modification in the initial distribution.

Elliot and Cameron[10] working on intensities of the first positive bands of N_2 have shown that the probability of transitions should be independent of the conditions of excitation. Such a conclusion, according to them is possible only if the proportionality factor is constant for all the bands having a common upper level. It is not likely that this will be a consequence of Franck-Condon principle which only governs the maximum transition probabilities. Taking our experiments with different gas/oxygen ratios as the five cases of excitation and calculating on the lines suggested by Elliot and Cameron,[10] we cannot trace any constancy in proportionality factors between intensities for bands having common upper level. This is evident from the horizontal rows of table IV, in which the factors calculated for some transitions with common upper level show wide departure from each other. It does not seem reasonable, therefore, to suppose that the probability of any transition is independent of the conditions of excitation, any such conclusion being true only as far as the maximum probabilities are concerned. This latter is a well-known consequence of Condon's theory and has been verified experimentally. As regards the probabilities of transition, it is not possible to predict them unless the theory of transition probabilities also takes into account the number of molecules in the initial levels.

TABLE IV.

Proportionality Factors.

Correlation factors for gas/oxygen ratios.

Transitions compared.	Gas/oxygen Ratios.				
	1·25	2	3	4	5
(1, 0) to (1, 1)	2·177	1·507	1·757	1·448	1·711
(1, 1) to (1, 2)	1·552	1·542	1·504	1·536	1·827
(1, 2) to (1, 3)	3·447	1·423	4·109	3·657	2·101
(2, 0) to (2, 1)	0·425	0·248	0·439	0·292	0·155
(2, 1) to (2, 2)	3·908	3·179	3·683	4·618	4·710
(2, 2) to (2, 3)	0·634	1·323	0·648	0·533	0·746
(2, 3) to (2, 4)	3·307	0·917	3·407	3·228	1·601
(3, 1) to (3, 2)	0·804	0·877	1·093	0·604	0·478
(3, 2) to (3, 4)	3·347	5·906	2·977	3·581	4·075
(3, 4) to (3, 5)	3·003	1·128	2·676	2·193	1·381

Out of the two expressions for potential energy quantitatively examined, we find better agreement of experimental values with the theoretical ones derived from the Rydberg's expression, a view which is in confirmity with that expressed by Tawde.[5] This occurs under all the cases studied and can be verified with reference to Figs. 1 to 5. This agreement is close specially in the branch $r_{min} \rightarrow r_{min}$, while the Morse expression gives transitions which deviate widely from experimental values in this branch. In the $r_{max} \rightarrow r_{max}$ branch both the Morse and Rydberg expressions give results which coincide.

An estimate of probability of various initial states is obtained by adding up the intensities under given values of v′. It appears that the maximum occurs at v′ = 0, there being a gradual fall for higher va[illegible] v′. The distribution of intensities about sequences shows that th[illegible] maximum occurs in the sequence v′—v″ = + 1 and there is a marked preponderance towards smaller values of Δv. This latter is a feature of many band spectra.

Whether the conditions examined approximate to low or high temperature distributions, we are led to conclude from the results that the distribution is definitely a high temperature one, as there is an increase of intensity as we pass away from the sequence with v′ = 0 towards the higher values of v′. Typical low temperature distribution is usually characterised by a rapid fall which is not experienced here.

To decide whether the distribution as obtained by exciting the bands in the oxy-coal gas flame is thermal or non-thermal in character, we can calculate by assuming the Bolzmann factor $e^{-\frac{E_{v'}}{kT}}$ the probabilities of occurrence of various sequences. These support the conclusion that the excitation in the present case is a thermal one as the bands (0, 0), (1, 0), (2, 0) appear approximately with relative intensities as expected from theoretical considerations.

The results of temperatures are such that definite conclusions cannot be drawn from them. The temperatures calculated range from 6200°K to 8200°K and this order is nowhere near the actual value which one should expect in the oxy-coal gas flame, within the range of gas/oxygen ratios examined. From thermal experiments, the temperature of oxy-coal gas flames should be somewhere about 2500° to 3000°K. The derivation of higher values means that molecules are not in statistical equilibrium in the upper vibrational states at the temperature of the source, a conclusion which confirms the previous observations of some of the authors. The spectroscopic results so far available point to the conclusion that Boltzmann distribution exists only in the case of arc. This is so from the results of Ornstein and Brinkman[8] and Tawde[11]. However, if one could examine the variation of the values of temperatures with the gas/oxygen ratios, one comes across a result which is similar to that found by Loomis and Perrott.[12] This has to be studied with reference to Fig. 6. The graph has a maximum between the ratios 3 and 4. But we have reasons to believe that this cannot be the real state of affairs as the maximum temperature from the size of the cone and the appearance of the flame should be attained somewhere between the ratios 2 and 3. The graph of Fig. 7 which gives the relation between the size of the cone and the gas/oxygen ratios has a minimum between the ratios 2 and 3 and this according to considerations of Thorpe[1] should correspond to maximum temperature in the flame.

We are unable to detect a regular relation between the positions of 'intensity centres' and the gas/oxygen ratios probably due to Boltzmann distribution being not attained, or the temperature variation from one gas/oxygen ratio to the other, may be of the order of errors, which is quite likely. It may however, be noted that intensity tends to shift to less refrangible side as the gas-oxygen ratio increases.

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SUMMARY

(1) Gross intensities of C_2 (Swan) system excited in oxy-coal gas flame with varying proportions of coal gas and oxygen, have been measured by the method of photographic photometry, using a standard lamp and calibrated step-slit.

(2) The transition probabilities have been derived from the potential energy curves using Morse's and Rydberg's expressions and compared with the experimental results.

(3) The effective temperatures for all the conditions are derived on the assumption of the statistical equilibrium of molecules in the initial vibrational levels. The results are discussed from various stand-points.

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MUTUAL COAGULATION OF COLLOIDAL SOLUTIONS
PART I—INTERACTION OF FERRIC HYDROXIDE AND PRUSSIAN BLUE SOLS

By

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INTRODUCTION

If an electrolyte is added to a colloidal solution, flocculation occurs as a result of preferential adsorption of the oppositely charged ions of the electrolyte on the colloidal particles. Similarly if two colloidal solutions with oppositely charged particles are mixed together, coagulation should occur under certain circumstances. It is known that if the particles of one of the sols are in a large excess, coagulation does not occur and the mixture, although more turbid, has the properties of the sol whose particles are in excess. Between the two limiting cases in which one or the other sol is in decided excess, there is an intermediate zone in which mixing completely or partially coagulates both the sols. Since coagulation can occur even when particles are not completely discharged, complete coagulation is observed not only at a definite ratio between the quantities of the two particles, but over a comparatively large range of different ratios.

The mechanism of mutual coagulation is, however, not very simple as the colloidal solutions besides having oppositely charged particles, also have peptising and other electrolytes (formed as a result of double decomposition during preparation of the sols). Under the circumstances when two colloidal solutions are mixed there will also be precipitation if the electrolytes present in the mixture form an insoluble salt. The electrolyte in each sol will also affect the distribution of ions in the double layer round the colloidal particles of the other sol when the two sols are mixed and thus alter their stability. Thus Weiser and Chapman (*J. Phys. Chem.*, 1931, *35*, 543 ; 1932, *36*, 714), came to the conclusion that the process of mutual coagulation may be determined by a number of factors, namely, (1) electric neutralisation of charge, (2) mutual adsorption of the colloidal particles, (3) interaction between stabilising ions, and (4) the presence of free electrolytes in the sols. Hazel and McQueen (*ibid.*, 1933, *37*, 571) have suggested from their experiments that a mechanism of mutual coagulation solely dependent upon chemical reactions between the stabilising ions or a simple preferential adsorption of one of these ions is improbable.

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* The experimental work has been carried out entirely by Mr. Y. S. Paranjpe under the direction of the other two authors.

In the present investigation mutual coagulation of colloidal ferric hydroxide (+ vely charged) and prussian blue (— vely charged) has been studied with reference to changes in the charge on the particles and decrease in the amount of electrolytes in the sols by having recourse to dialysis.

EXPERIMENTAL

Colloidal ferric hydroxide was prepared in the same manner as done by Desai and Borker (*Trans. Faraday Soc.*, 1933, *29*, 1269) and prussian blue by the method used by Mankodi, Barve and Desai (*Proc. Indian Acad. Sc.*, 1936, *4*, 480). Dialysis was carried out in parchment paper bags as usual and the cataphoretic speed (cat. speed) determined exactly in the same manner as done by Desai and co-workers (*loc. cit.*).

By a large number of preliminary experiments it was found possible to fix up the concentration of the colloids and the rate of dialysis such that both the sols have comparable coagulating concentrations and the dialysis (purification of the sols) proceeds at nearly the same rate.

The following procedure was adopted for locating the zone of complete mutual coagulation :

The two sols were mixed in a uniform manner in such amounts that the total volume was 10 c.c. By increasing the amount of one colloid and correspondingly decreasing the amount of the other, it was found that upto a particular value of the ratio of the two colloids there was no turbidity at all. Thereafter the turbidity appeared (turbidity in this case is only due to flocculation and not due to precipitation of an insoluble salt) and continued over some range and then again at some other ratio of the amounts of the two colloids, the mixture became clear. The zone of coagulation thus corresponds to the range between these two limits. The range could be determined correct upto 0·1 c.c. of a colloid without any difficulty. In each case the appearance of turbidity was determined by looking through the test tube at a dark translucent screen covered with white lines. The point at which the lines became indistinct was considered as the standard turbidity in each case. Similarly when the lines became distinct it was taken that the turbidity had disappeared.

It was found that the turbidity which appeared due to mutual coagulation migrated on cataphoresis towards that pole whose charge was opposite in sign to that of the particles of the sol present in excess. Over the range of mutual coagulation the cat. speed continuously decreased and reached a zero value after which the turbidity on adding increasing amount of the oppositely charged colloid began to move towards the other pole.

No change in the width or the location of the zone was detected either when prussian blue sol was added to ferric hydroxide or vice versa.

The temperature of the experiments was kept at 30°C.

RESULTS

The results of mutual coagulation are given in Table I.

TABLE I.

Mutual precipitation of Ferric hydroxide by Prussian blue, both of varying purity. Numbers in the different columns refer to c.c. of Ferric hydroxide in 10 c.c. of the mixture of ferric hydroxide and prussian blue.

Days of dialysis of Ferric hydroxide	Days of dialysis of Prussian blue.																				
	0			4			7			11			15			18			23		
	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D
0	1·5	6·6	8·1	1·1	6·4	7·5	0·5	6·2	6·7	3·5	1·4	4·9	0·1	0·6	0·7	0·1	1·0	1·1	0·02	1·48	1·50
4	0·3	8·4	8·7	1·9	6·5	8·4	2·8	6·4	9·0	2·9	2·4	5·3	0·4	0·7	1·1	0·2	1·0	1·2	0·15	1·95	2·10
7	0·9	8·9	9·8	0·9	8·1	9·0	2·1	6·4	8·5	0·9	3·5	4·4	0·8	0·4	1·2	0·2	1·3	1·5	0·25	2·15	2·40
11	1·1	8·7	9·8	1·3	7·4	8·7	1·6	6·7	8·3	0·9	4·6	5·5	1·2	2·1	3·3	0·2	2·8	3·0	0·30	2·50	2·80
15	0·8	9·1	9·9	0·8	8·7	9·5	0·7	8·2	8·9	0·7	7·1	7·8	3·5	0·1	3·6	0·5	3·7	4·2	0·40	4·60	5·00
18	1·1	8·8	9·9	0·7	9·0	9·7	0·7	8·6	9·3	0·5	8·5	9·0	0·5	6·3	6·8	0·3	6·5	6·8	0·50	5·75	6·25
23	1·1	8·8	9·9	0·8	8·8	9·6	0·7	8·8	9·5	0·5	8·8	9·3	0·5	7·4	7·9	0·5	7·6	8·1	0·55	7·70	8·25

A = Appearance of turbidity.
Z = Zone of precipitation.
D = Disappearance of turbidity.

The results for sols dialysed for the same periods taken from Table I (the A and D values) are plotted in Fig. 1. Fig. 1 thus gives the width as well as the position of the zone of mutual coagu-

lation (shaded portion) at different periods of dialysis, *i.e.*, different stages of purity of the sols.

The cat. speed results of the two sols are also plotted in Fig. 1 curves 1 and 2 being for prussian blue and ferric hydroxide, respectively.

DISCUSSION

It will appear from Fig. 1 that the cat. speed, *i.e.*, the charge on the colloidal particles of both the sols first increases, reaches a maximum and then decreases with the progress of dialysis. These results are exactly similar to those obtained by Desai and co-workers (*loc. cit.*). The changes in charge during dialysis have been explained by Desai and co-workers by assuming that the process of dialysis can be taken roughly as a reverse of the process of adding small increasing amounts of the peptising agent to the colloid so far as the influence of the electrolyte on the cat. speed is concerned. Thus as the amount of the peptising electrolyte in the intermicellary liquid continuously decreases during dialysis, some of the oppositely charged ions, which are bound with the preferentially adsorbed similarly charged or primarily adsorbed ions as a result of electrical adsorption, will become free as their concentration in the sol diminishes. This process will result in an increase in charge on the colloidal particles as the charge is due to those primarily adsorbed ions which are uncovered, i.e., are free, the oppositely charged ions being away in the outer sheet of the double layer. At the same time the chances for the desorption of the preferentially adsorbed similarly charged or primarily adsorbed ions from the surface of the particles, i.e., from the inner sheet of the double layer will also increase as their concentration in the intermicellary liquid diminishes; the charge will decrease due to this effect. The primarily adsorbed ions being however strongly adsorbed as a result of chemical affinity, their desorption will occur only when their concentration in the intermicellary liquid becomes very low during dialysis, i.e., only in the later stages of dialysis (after 15 days in the present instance).

From Table I it will appear that the changes in the range within which mutual coagulation takes place when to one of the sols dialysed for a certain period another sol dialysed for different periods is added are not quite regular (changes in values of 'Z' in any vertical column or any horizontal row of the table). This is due to the fact that the sol dialysed for different periods has varying amounts of electrolytes, which affect the other sol dialysed for any fixed period in different ways. The process of charge neutralisation being complex in these cases, there are no regular variations in the values of 'Z'.

It will however appear that if we consider the mutual coagulation of both the sols dialysed for the same periods (underlined values in Table I), there is a striking regularity in the variation of the width of the zone, i.e., the values of 'Z'. The width of the zone of mutual coagulation is largest for the impure sols (0 day dialysis—Z = 6·6 units) and the long period dialysed sols (23 days dialysis—Z = 7·7 units) and is minimum (Z = 0·1 units) for both the sols dialysed for 15 days. In other words the range within which mutual coagulation occurs on mixing the two sols is smallest for sols dialysed for 15 days and larger than that value for sols dialysed for periods shorter or longer than that period. Since the charge in both the cases first increases and then decreases (Fig. 1) during dialysis, the width of the zone first decreasing and then increasing at the same time. Thus it appears that there is some relation between the variation in the charge on the colloidal particles of the two sols and the width of the zone of the mutual coagulation. In what follows the relation between the charge on the particles and the width of the zone will be discussed.

Of the four factors which have been considered by Weiser and Chapman (*loc. cit.*) as being responsible for mutual coagulation, the one due to the interaction of the stabilising ions is inoperative in the present case as both the sols are acidic, one due to the presence of hydrochloric acid and the other due to the presence of oxalic acid. The effect of impurities in the colloids will be most pronounced for undialysed sols when both of them contain appreciable amounts of the electrolytes and will decrease with the progress of dialysis, being minimum when the sols are pure. Regarding the mutual adsorption of the oppositely charged particles of one sol by those of the other, it is certain that its effect will be to neutralise the charge. In fact the greater the charge on the particles of both the sols, the greater will be the attraction between them due to electrostatic forces and hence the greater the mutual adsorption. The mutual adsorption of the oppositely charged particles of one sol by those of the other will first increase and then decrease due to changes in charge during dialysis. The fourth factor that is, the neutralisation of electric charge on the particles of the two sols will depend upon the adsorbability of the oppositely charged ions of the electrolytes by the particles of each sol in the mixture as well as on the mutual adsorption of the oppositely charged particles of one sol by those of the other. The neutralisation of the charge due to adsorption of oppositely charged ions from the mixture will be progressively decreasing during dialysis as the amounts of different electrolytes continuously decrease, while that due to mutual adsorption will first increase and then decrease.

Generally speaking the greater the charge on the particles the greater the forces of repulsion between them and the greater the stability of the sol. It should, however, be mentioned that the stability of the sol as determined by flocculation values with electrolytes does not always go hand in hand with the charge because of the complications introduced by electrolytic impurities initially present in the sol as shown by Desai and co-workers (*loc. cit.*). The sols begin to coagulate on mixing as soon as the charge on the particles of either of them is reduced in the manner contemplated above to such a limit that the kinetic energy of the particles exceeds the work of repulsion, thereby allowing the particles to approach sufficiently near for the action of cohesive forces. The aggregates formed may contain either particles of the same substance as in the case of coagulation of any one sol on addition of electrolytes if the charge has been reduced as a result of electrical adsorption of the oppositely charged ions in the mixture or particles of both the sols if the charge has been reduced as a result of mutual electrical adsorption or a mixture of both the type of particles.

Now if a sol with a high charge on its particles and hence having great stability is to be coagulated by the oppositely charged colloid, (considering that the charge reduction takes place only as a result of mutual adsorption), the amount of the latter will have to be sufficiently large to lower down the charge to such a value that aggregation can take place as mentioned above, producing turbidity. Similarly the disappearance of the turbidity or its appearance from the other end (i.e., when the second colloid is in excess) will occur only when there is large amount of the coagulating colloid from that end. As a result of this the zone of precipitation will be narrowest or the value of 'Z' will be lowest when the particles of both the sols have greatest charge. On the other hand if the charge on the particles is low, the coagulation will begin at a low concentration of the other colloid as the charge will have to be reduced only slightly for allowing coalescence to take place. Similarly the appearance of turbidity from the other end will also be at a low concentration of the other colloid. In this case the zone of precipitation will be relatively large. Thus the sols whose particles have smallest charge, i.e., undialysed (0 day dialysis) or highly purified sols (23 days dialysis) will have largest zone of mutual coagulation.

In the above paragraph the variations in the width of the zone have been considered on the basis that the reduction in charge to allow coalescence to take place and to produce turbidity, occurs as a result of mutual adsorption alone. As mentioned before the reduction in charge will also take place due to electrical adsorption of the oppositely charged ions of the electrolytes in the mixture. In the case of undialysed sols as the amounts of electrolytes in them are appreciable, even small concentrations will also reduce the charge to such a value that coalescence can take place, the electrical adsorption of the oppositely charged ions of the electrolyte in the mixture being strong. Thus the width of the zone of mutual coagulation will be largest for undialysed sols. With the progress of dialysis as the amounts of electrolytes in the sol decrease, higher concentrations will be required for producing the same degree of turbidity and hence the width of the zone of mutual coagulation will continuously decrease. If the effect of electrolytic impurities is alone responsible for the changes in the width of the zone, the width should be smallest for highly purified sols. But as will be seen from Table I, the value of 'Z' decreases only upto 15 days of dialysis and increases thereafter. It is therefore clear that upto 15 days of dialysis, i.e., till the maximum value of charge and the lowest value of 'Z' is reached, the effect of both mutual adsorption and electrolytic impurities should be considered, while the mutual adsorption alone is important for increase in the value of 'Z' for sols dialysed for periods longer than fifteen days.

Our results do not support the generalisation of Weiser and Chapman (*loc. cit.*) that the zone of mutual coagulation is quite narrow if both the sols contain little or no free electrolyte although their other generalisation that the zone is widest for impure sols is supported; it should, however, be mentioned that even in the latter case the mutual adsorption has to be considered as controlling the width of the zone besides the electrolytic impurities. The difference between our observations and those of Weiser and Chapman is probably due to a difference in the nature of the colloids investigated and the purity of the sols.

SUMMARY

Mutual coagulation of ferric hydroxide and prussian blue sols with the progress of dialysis has been studied with reference to changes in charge on the particles during dialysis. It is observed that with progress of dialysis the width of the zone of mutual coagulation first decreases and then increases, the charge on the particles of the two sols first increasing and then decreasing at the same time. The results are discussed from the point of view of changes in the mutual adsorption of the oppositely charged particles of one sol by those of the other and in the amount of electrolytic impurities during dialysis.

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THE ACTION OF NITRIC ACID ON MERCURY—PART I.

By

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The action of nitric acid on metals has attracted the attention of chemists since a long time and although much intensive work has been done and many working hypotheses have been developed, a complete satisfactory explanation of the mechanism of the process has not yet been arrived at (Bancroft, *J. Phys. Chem.*, 1924, 28, 475; Milligan and Gillette, *ibid.*, 1924, *28,* 744; Palit and Dhar. *Zeit. anorg. Chem.*, 1924, *134,* 191; *Dhar, J. Phys. Chem.*, 1925, *29,* 142). In the present work attempts have been made to elucidate the mechanism of the action of nitric acid on mercury.

The action of nitric acid on mercury has been studied by a number of workers. Millon (*Compt. rend.*, 1842, 14, 904) noted that purified nitric acid acts on mercury only when a reducing agent is present, and according to Divers (*J. C. S.*, 1886, *43,* 443) and Veley (*Proc. Roy. Soc.*, 1891, 48, 458) nitric acid freed from nitrous acid has no action on mercury.

Montemartini (*Gazz. Chim. Ital.*, 1892, 22, 397) showed that when mercury is allowed to react with nitric acid, the quantity of nitric oxide produced diminishes as the concentration increases and with strong acids nitrogen tetroxide is evolved. Moreover, the product of the interaction with 25 per cent nitric acid is mercurous nitrate while with 50 to 70 per cent acid mercuric salts are obtained.

Ray (*Zeit. anorg Chem.*, 1896, 12, 365; *J. C. S.*, 1897, 71, 337; 1905, 87, 171) studied the action of nitric acid on mercury in detail and observed that when mercury is covered by a 10 cm. layer of nitric acid (S. G. 1·11 at 15°) at 30°-35°, bright yellow crystals of mercurous nitrite are freely formed. A part of the nitric acid is reduced to nitrous acid in the beginning, and some mercurous nitrite produced in the interaction is decomposed by the nitric acid with the result that the proportion of nitrous acid in the solution rapidly increases until mercurous nitrite and mercurous nitrate accumulate in equimolecular proportions; the proportion of nitrous acid in solution then remains constant and nitrous acid acts as a catalytic agent in the reaction between mercury and nitric acid : $2\ Hg + 2\ HNO_3 =$

$HgNO_3 + HgNO_2 + H_2O$. Further, the reaction leads to the formation of the following salts: $Hg_2(NO_2)_2$; $Hg_2(NO_3)_2$; $Hg_2(NO_3)_2$, 2HgO; HO. Hg_2NO_3; $Hg_2(NO_3)_2$, HO. Hg_2NO_3; $Hg_2(NO_3)_2$, 4 HO. Hg_2NO_3; HgO, 2 HO. Hg_2NO_3; HgO, HO. $HgNO_3$, HO. Hg_2NO_3; $Hg(NO_3)_2$ aq.

Stansbie (*J. Soc. Chem. Ind.*, 1913, 32, 1135,) showed that nitric acid dissolves mercury more readily when the metal and nitric acid are at rest than when the metal is rotated or the acid is stirred. Thus the dissolution of mercury not only depends on the presence of nitrous acid but also on the accumulation of nitrite in the neighbourhood of the affected mercury. Further, it was shown that the speed of the reaction is increased by the proportion of nitrite present and is decreased when the nitrite is converted into nitrate by boiling.

Palit and Dhar (*loc. cit.*) studied the action of (*i*) ordinary nitric acid, (*ii*) distilled nitric acid and (*iii*) nitric acid distilled over urea, on mercury and concluded that the interaction is independent of the nature of nitric acid used, although it was found that nitric acid distilled over urea had generally the least power of dissolving mercury. According to these workers, the first product of the action of nitric acid on mercury is mercurous nitrite which is formed in greatest quantity by the use of 26 per cent nitric acid at 30°. The yield of mercurous nitrite is greatly increased in presence of mercurous nitrate or ferric nitrate, but no mercurous nitrite is formed if sodium nitrite or urea is added to the nitric acid or if the temperature is allowed to rise above 52°. In presence of sodium nitrite, nitric acid interacts readily with mercury in the cold giving a complex sodium mercuric nitrite, whilst in presence of urea it has very little action on the metal.

The influence of various substances on the action of nitric acid on mercury, has been studied by Acworth (*J. C. S.*, 1875, *28*, 828), Millon (*loc. cit.*), Veley (*Phil. Trans.*, 1891, 182, A. 279), Ray (*J. C. S.*, 1911, 99, 1012), Banerji and Dhar (Zeit. anorg. Chem., 1922, 122, 73) and Palit and Dhar (*loc. cit.*). Acworth found that in presence of ammonium nitrate nitrogen is the chief product of the reaction between mercury and nitric acid. According to Millon, Veley and Ray, the presence of ferric sulphate or nitrate removes nitrous acid from nitric acid as fast as it is formed and hence inhibits the reaction. Ray found that the interaction between mercury and nitric acid is accelerated by manganese nitrate or sodium nitrate, while the sulphates of manganese, sodium or potassium neither accelerate nor retard it. Banerji and Dhar, and so also Palit and Dhar, observed that the presence of ferrous sulphate accelerates the dissolution of mercury in nitric acid owing to the formation of nitrous acid, either by direct reduction of nitric acid by ferrous sulphate or by the intermediate formation of the nitric oxide-ferrous sulphate complex which then yields nitrous acid : $HNO_3 + 2\ NO + H_2O = 3\ HNO_2$, whilst the presence of ferric nitrate retards the reaction between mercury and nitric acid. Banerji and Dhar also noted that sodium nitrate, manganese nitrate, potassium chlorate and potassium permanganate have the retarding effect on the rate of dissolution of mercury in nitric acid, whereas Palit and Dhar in subsequent work (*J. Phys. Chem.*, 1926, 30, 1125) observed the efficiency of various nitrates, e.g., mercurous nitrate, ferric nitrate, manganous nitrate, nickelous nitrate, etc., on the formation of mercurous nitrite by the action of nitric acid on mercury as in the order given.

According to Klemenc (*Zeit. Electrochemie*, 1926, 32, 150) the formation of mercurous nitrite in the action of nitric acid on mercury may be explained by the existence of the equilibrium : $2\ HgNO_3 + NO_2 = Hg_2N_3O_8$ in a diffusion layer near the surface of the metal, the mercury compound $Hg_2N_3O_8$ diffusing away from the metal and getting decomposed according to the equation, $2\ Hg_2N_3O_8 + H_2O = HgNO_2 + 3\ HgNO_3 + 2\ HNO_3$.

In the work described below, the interaction between mercury and nitric acid has been studied by conducting experiments under varying conditions and examining quantitatively, at the end of each experiment, the gaseous products as well as substances in solution.

EXPERIMENTAL

Materials

Mercury. Merck's extra pure mercury was passed repeatedly in the form of small globules through a long column of dilute nitric acid (S. G. 1·1), dried and distilled in vacuo : the middle fraction was collected and used in all experiments.

Nitric Acid. Merck's extra pure nitric acid was taken for preparing 1, 2, 3, 4 and 5 N solutions and the latter were used after standardisation with alkali.

Merck's extra pure *sodium nitrite* and *urea* were used after recrystallisation from water, while *mercurous nitrate* used was of Kahlbaum's make. *Mercurous nitrite* was prepared according to Ray's method (J. C. S., 1897, 71, 337) and *mercuric nitrate* was obtained from Kahlbaum's basic nitrate of mercury by treatment with fuming nitric acid.

Apparatus and Procedure

In all experiments described below, the apparatus shown in Fig. 1 was used. The reaction vessel having a bulb A of 40 c.c. capacity and a side ground joint arrangement B to introduce a small tube 't' was connected with the spiral C through a ground joint 's' and a tap 'm' and the whole put in communication with the manometer E and the Sprengel pump, through a U-tube D containing a saturated solution of sodium hydroxide and taps 'n' and 'o'. After introducing acid (10 c.c.) of a definite concentration in the bulb A and adjusting the small tube 't' containing a weighed amount of mercury with or without urea or sodium nitrite as shown in the figure, the apparatus was evacuated, and the system tested for leak by allowing it to stand overnight.

The nitric acid bulb was next immersed in a water bath maintained at a constant temperature, the taps 'm', 'n' and 'o' were closed and the experiment was started by tilting the reaction vessel with the help of the spiral C and allowing the tube 't' together with its contents to fall in the nitric acid. The spiral decreased the rigidity of the apparatus and enabled the contents of the bulb A to be shaken in vacuo whenever required.

At the end of the experiment the taps 'm' and 'n' were opened, the evolved gas was allowed to stand in contact with sodium hydroxide of the U-tube D and the unabsorbable gas, if any, collected by means of the Sprengel pump after opening the tap 'o' and analysed. The apparatus was then disconnected and (*i*) the contents of the bulb A were examined for free mercury, mercurous and mercuric mercury and nitrite, and (*ii*) the contents of the U-tube were examined for nitrite and nitrate. In (*i*) free mercury, if any, was filtered off, washed, dried over phosphorous pentoxide at room temperature and weighed, and the filtrate together with washings diluted to 100 c.c. Mercurous mercury was estimated as mercurous chloride by treating the solution with a slight excess of 0·1 N sodium chloride solution, and the mother liquor obtained after the removal of mercurous chloride used for the estimation of mercuric mercury and nitrite. Mercuric mercury was estimated as mercuric sulphide by treatment with a freshly prepared hydrogen sulphide solution and the nitrite by titration with standard potassium permanganate solution. In (*ii*) the solution after dilution to 100 c.c. was analysed for nitrite and nitrate by the permanganate and ferrous sulphate methods respectively. The amount of nitrate present was found out by determining the total nitrate in the solution left after oxidation with potassium permanganate and subtracting the calculated amount of nitrate corresponding to the amount of nitrite found.

All the experiments described in the paper were repeated several times and only the mean values have been given in the tables.

(a) ***Experiments with mercury and nitric acid of different concentrations.***

In order to find the suitable concentration of nitric acid for a detailed investigation of the action of nitric acid on mercury, experiments were first undertaken with mercury (1 g.) and nitric acid (10 c.c.) of different concentrations i.e., 1, 2, 3, 4 and 5 N solutions at 25° for a period of 24 hours. The results of these experiments are given in Table I.

Experiments with mercury (1g.) and nitric acid (10 c.c.) of different normalities at 25° for a period of 24 hours.

Table I.

HNO_3 N	Mercury taken g.	Free Hg g.	(Dissolved)-Acid solution			Alkali solution			Nitric oxide (N.T.P.)	
			$Hg^{\cdot}$ g.	$Hg^{\cdot\cdot}$ g.	NO_2' g.	NO_2' c. c. 0·1 N $KMnO_4$	NO_3' c. c. 0.1N $FeSO_4$	N_2O_3 g.	c.c.	g.
1	1.0000	0.9948	...	...	...	...	...	...	...	...
2	1.0000	0.5520	0.3949	0.0503	0.0805	1.5	2.2	0.0028	7.5	0.0104
3	1.0000	0.2125	0.6475	0.1478	0.0690	1.6	2.3	0.0030	16.8	0.0225
4	1.0020	...	0.3146	0.6804	0.0943	3.3	4.9	0.0063	24.6	0.0330
5	0.9998	...	...	0.9870	0.0897	10.0	14.8	0.0189	20.1	0.0270

The above results show that

(*i*) mercury is not affected by 1 N nitric acid, but is affected by nitric acid of higher concentrations ;

(*ii*) in experiments with 2 N and 3 N nitric acid some mercury remains unchanged and its amount is less in experiments with 3 N nitric acid than in experiments with 2 N nitric acid, whereas in experiments with 4 N and 5 N nitric acid all mercury passes in solution ;

(*iii*) the amount of mercurous mercury in experiments with 3 N nitric acid is higher than the amount of mercurous mercury in experiments with either 2 N or 4 N nitric acid, and it is altogether absent in experiment with 5 N nitric acid ; whereas the amount of mercuric mercury goes on increasing with an increase in the concentration of nitric acid ;

(*iv*) the amount of nitrite in the acid solution is practically constant in all experiments;

(*v*) the gas evolved in all experiments consists of nitric oxide. Some nitrogen tetroxide is also evolved along with nitric oxide and its amount increases with the increase in the concentration of nitric acid;

(*vi*) the total amount of nitrite, nitric oxide and nitrogen tetroxide is proportional to the amount of mercury passing in solution as mercurous and mercuric mercury.

It will be seen from the above experiments that mercury tends to react with 2 N or more than 2 N nitric acid forming nitrites and nitrates of mercury along with the evolution of nitric oxide and some nitrogen tetroxide. The facts that

(1) the amount of mercurous mercury increases so long as free mercury is present and then diminishes in absence of free mercury.

(2) the amount of mercuric mercury which is low in presence of free mercury suddenly increases when free mercury is absent, and

(3) the total amount of nitrite, nitric oxide and nitrogen tetroxide is proportional to the amount of mercury passing in solution,

show that the interaction leads to the production of either mercurous or mercuric mercury and nitrite which may be present as nitrous acid or as such may be reacting with nitric acid giving nitrate and nitrous acid. A part of the latter then breaks up giving nitric acid and nitric oxide according to 3 $HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$, or interacts with nitric acid, if the concentration of nitric acid be high, evolving nitrogen tetroxide as $HNO_2 + HNO_3 \rightarrow N_2O_4 + H_2O$. (cf. Ray, *loc. cit.*; Palit and Dhar, *loc. cit.*)

(b) *Experiments with mercury and 4 N nitric acid (i) for different periods of time and (ii) at different temperatures.*

Since all mercury is affected by 4 N nitric acid at 25° within 24 hours with the formation of mercurous and mercuric salts in solution, experiments were next conducted with mercury (1 g.) and 4 N nitric acid (10 c.c.) (*i*) for different periods of time i.e., 2, 4, 8, 12... 40 h[illegible]at 25° and (*ii*) at different temperatures i.e., 5°, 15°, 25°, [illegible], and 45° for a period of 24 hours. The results of these experiments are given in Tables II and III respectively.

(*i*) *Experiments with mercury (1 g.) and 4 N nitric acid (10 c.c.) at 25° for different periods of time.*

Table II.

Time in hours	Mercury taken	Free Hg˙	(Dissolved)-Acid solution			Alkali solution			Nitric oxide (N. T. P.)	
			Hg˙˙	Hg˙	NO_2'	NO_2' c c. 0. 1N $KMnO_4$	NO_3' c.c. 0. 1 N $FeSO_4$	N_2O_3		
	g.	g.	g.	g.	g.			g.	c.c.	g.
2	1.0000	0.7645	0.2250	...	0.0138	...	...	...	5.0	0.0066
4	1.0005	0.6970	0.2781	0.0200	not estimated	...	...	...	3.5	0.0053
8	1.0000	0.2310	0.6497	0.1150	0.0390	...	...	...	10.2	0.0134
12	[illegible]	0.0220	0.6109	0.3650	0.0460	1.5	2.3	0.0028	13.0	0.0174
16	1.[illegible]	...	0.4753	0.5129	0.0759	2.0	3.1	0.0038	14.8	0.0200
18	1.0000	...	0.4173	0.5700	0.0789	2.2	3.2	0.0042	14.0	0.0180
24	1.0000	...	0.3146	0.6804	0.0945	3.3	4.9	0.0063	24.5	0.0330
40	1.0040	...	0·1100	0.8840	0.1150	5.0	7.6	0.0095	13.2	0.0174

The above results show that

(*i*) almost all mercury passes in solution when the reaction has proceeded for 12 hours;

(*ii*) the production of mercurous mercury goes on increasing so long as free mercury is present and then diminishes gradually, whereas the formation of mercuric mercury which is low in the first few hours goes on increasing steadily afterwards;

(*iii*) the formation of nitrite and the evolution of gas which mainly consists of nitric oxide are proportional to the amount of mercury passing in solution both as mercurous and mercuric mercury;

(*iv*) the dissolution of mercury in nitric acid as mercurous mercury in the first few hours is followed by the oxidation of mercurous mercury to mercuric mercury and both these reactions lead to the formation of nitrite in solution and the evolution of nitric oxide together with a little nitrogen tetroxide.

(ii) Experiments with mercury (1 g.) and 4 N nitric acid (10 c.c.) at different temperatures for a period of 24 hours.

Table III.

Temp. °C.	Mercury taken g.	Free Hg. g.	(Dissolved)-Acid solution.			Alkali solution.			Nitric oxide (N.T.P.)	
			$Hg^{\cdot}$ g.	$Hg^{\cdot\cdot}$ g.	NO_2' g.	NO_2' c.c. 0.1N $KMnO_4$	NO_3' c.c. 0.1 N $FeSO_4$	N_2O_3 g.	c.c.	g.
5	0·9990	0.5062	0.4430	0.0300	0.0180	...	...	...	5·9	0.0080
15	1.0007	0.0455	0.6857	0.2568	0.0368	2.0	3.1	0.0038	21.1	0.0280
25	1.0000	...	0.3146	0.6804	0.0943	3.3	4.9	0.0063	24.6	0.0330
35	1.0025	...	0.0467	0.9360	0.1081	5.6	8.6	0.0105	20.4	0.0270
45	0.9998	...	...	0.9915	0.1311	5.1	7.6	0.00[illegible]	[illegible]	0.0430

The above results show that

(*i*) the interaction between mercury and nitric acid which is slow at 5° proceeds rapidly with the rise in temperature and almost all mercury dissolves at and above 15° ;

(*ii*) the amount of mercurous mercury in experiments at 15° is higher than that in experiments at 5° or 25° or 35° and is absent in experiments at 45°, whereas the amount of mercuric mercury which is low in presence of free mercury in experiments at 5° goes on increasing steadily in experiments at higher temperatures, in experiments at 45° all mercury being held in solution as mercuric salt ;

(*iii*) the amounts of nitrate, nitric oxide and nitrogen tetroxide taken together increase steadily with the rise in temperature and are proportional to the amount of mercury passing in solution both as mercurous and mercuric mercury ;

(*iv*) the dissolution of mercury in nitric acid as mercurous mercury is followed by oxidation of mercurous mercury to mercuric mercury, and both these reactions lead to the formation of nitrite in solution and the evolution of nitric oxide together with traces of nitrogen tetroxide.

From the above results it may be concluded that the production of nitrite and nitric oxide in the interaction between mercury and nitric acid is from *two* reactions : (1) the dissolution of mercury in nitric acid as mercurous mercury and (2) the oxidation of mercurous mercury to mercuric mercury. It appears, therefore, highly probable that the initial stage of the interaction consists of the formation of mercurous mercury and nitrous acid, the latter yielding (*i*) nitric acid and nitric oxide according $3\ HNO_2 \rightleftharpoons HNO_3 + 2\ NO + H_2O$, and (*ii*) nitrogen tetroxide as $HNO_2 + HNO_3 \rightleftharpoons N_2O_4 + H_2O$.

(c) *Experiments with varying amounts of mercury and 4 N nitric acid.*

With a view to obtain further information regarding the nature of the initial product of the action of nitric acid on mercury, experiments were conducted with varying amounts of mercury i.e., 0·5, 1, 1·5, 2, and 2·5 g. and 4 N nitric acid (10 c.c.) at 25° for a period of 24 hours. The results of these experiments are given below in Table IV and represented graphically in Figs. 2 and 3.

Experiments with varying amounts of mercury and 4 N nitric acid at 25° for a period of 24 hours.

Table IV.

Mercury taken g.	Free Hg g.	(Dissolved)—Acid solution			Alkali solution			Nitric oxide (N.T.P.)	
		$Hg^{\cdot}$ g.	$Hg^{\cdot\cdot}$ g.	NO_2' g.	NO_2' c. c. 0.1N KMnO4	NO_3' c. c. 0.1N $FeSO_4$	N_2O_3 g.	c. c.	g.
0 5000	—	0.1209	0.3794	0.0460	0.4	(trace)	(trace)	10.8	0.0145
1.0000	—	0.3146	0.6804	0.0940	5.3	4.9	0.0063	24.6	0.0330
1.5000	—	0.5085	0.9990	0.1357	2.7	4.1	0.0052	24·3	0.0330
2.0000	—	0.8536	1.1430	0.1771	3.1	4.7	0.0059	20.2	0.0271
*2.5000	—	1.3160	1.1800	0.2220	2.9	4.6	0.0053	26.2	0.0337

* Yellow crystals of mercurous nitrite separated in this experiment.

The above results show that

(i) at 25°, 4 N nitric acid (10 c.c.) affects all the mercury up to 2·5 g.;

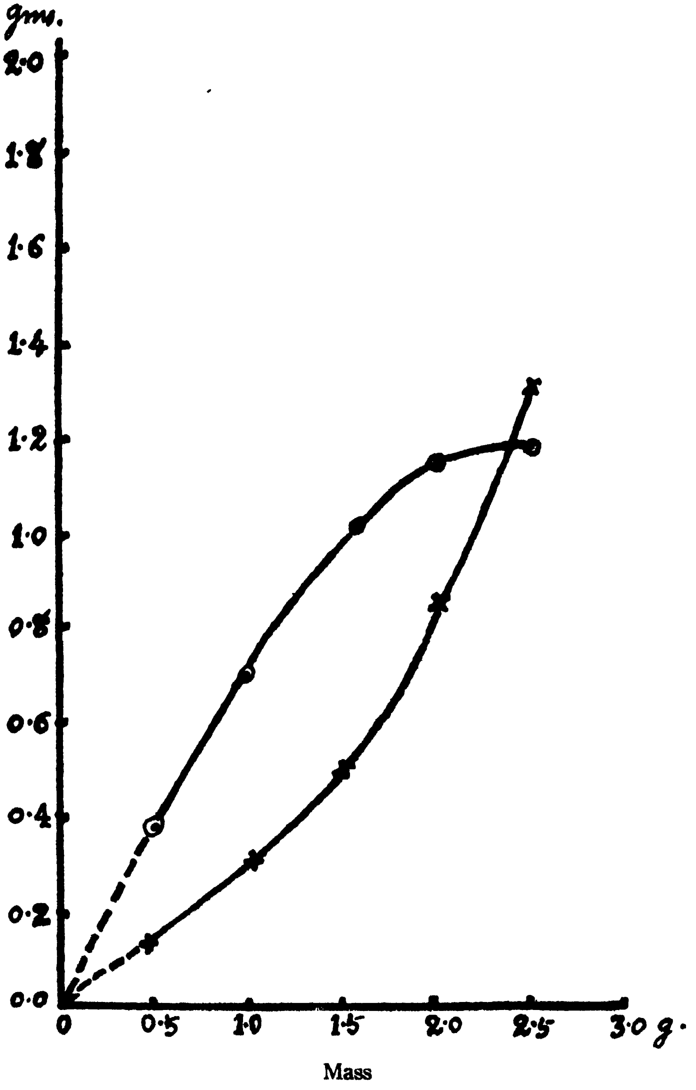
(ii) with the increasing amounts of mercury taken,

(a) the amount of mercurous mercury goes on increasing while the amount of mercuric mercury which also increases ultimately remains constant,

(b) the amount of nitrite increases regularly, and

(c) the evolved gas consists of nitric oxide ;

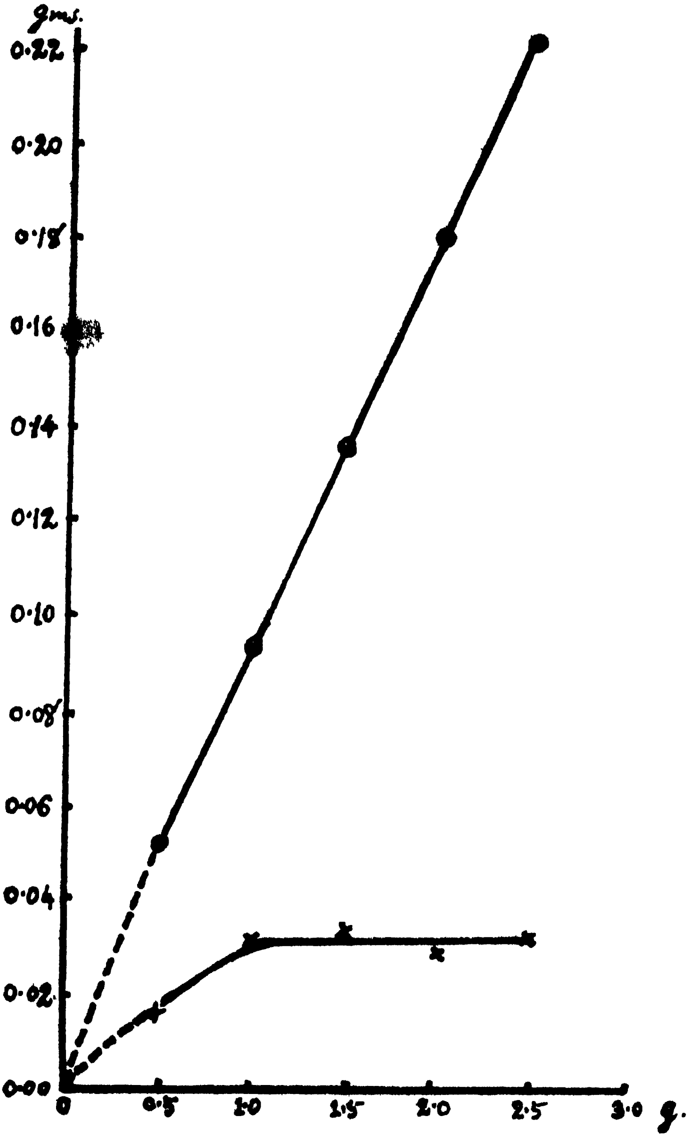
(iii) yellow crystals of mercurous nitrite tend to separate when the amount of mercury used in the experiment is large.



× $Hg^{\cdot}$ Mercury ⊙ $Hg^{\cdot\cdot}$ Mercury (×, ⊙ in solution)

Fig. 2.

Thus from the above experiments it appears that the production of mercurous mercury and nitrite increases in quantity in proportion to the amount of mercury used in the experiment, and that mercurous nitrite tends to separate over mercury when the concentrations of mercurous mercury and nitrite are fairly high.



Mass

⊙ NO₂ in solution. × No gas

Fig. 3.

Influence of (i) *urea and* (ii) *sodium nitrite on the action of nitric acid on mercury.*

In order to find whether the initial stage of the interaction involves the reaction with nitric acid or nitrous acid the influence of (i) urea, and (ii) sodium nitrite on the action of 4 N and 5 N nitric acid on mercury was next studied. As urea would eliminate nitrous acid (if present in traces in the nitric acid used or if produced in the interaction) according to $CO(NH_2)_2+2\ HNO_2= 2N_2+CO_2+3H_2O$, and as sodium nitrite would increase the concentration of nitrous acid in the nitric acid used, it was expected that the results would show how far the initial and subsequent stages of the interaction depend upon nitric acid and nitrous acid. The results of these experiments are given in Tables V and VI respectively.

(i) *Experiments with mercury (1 g.) and 4 N & 5 N Nitric acid (10 c.c.) in presence of urea at 25° for a period of 24 hours.*

Table V.

HNO_3	Urea added	Mercury taken	Free Hg.	(Dissolved)—Acid solution.			Alkali solution.			Nitrogen (N. T. P.)	
				$Hg^{\cdot}$	$Hg^{\cdot\cdot}$	NO_2'	NO_2' c.c. 0·1N $KMnO_4$	NO_3' c.c. 0·1N $FeSO_4$	N_2O_3	c.c.	
g.	g.	g.	g.	g.	g.	g.			g.		g.
4	0·1000	1·0000	0·9955	—	—	—	—	—	—	1·0	0·0012
4	0·2000	1·0000	0·9885	0·0100	—	—	—	—	—	1·0	0·0012
4	0·3000	1·0000	0·9930	—	—	—	—	—	—	1·0	0·0012
5	0·1000	1·0020	0·9890	0·0150	—	—	—	—	—	4·0	0·0050
5	0·2000	1·0140	0·9950	0·0140	—	—	—	—	—	4·2	0·0052
5	0·3000	1·0000	0·9720	0·0180	—	—	—	—	—	4·3	0·0054

The above results show that

(*i*) in presence of urea mercury does not interact to any appreciable extent with 4 N and 5 N nitric acid in agreement with the views of Divers (*loc. cit.*) and Veley (*loc. cit.*);

(ii) the gas evolved in these experiments consists of nitrogen.

It appears from the above experiments that Merck's extra pure nitric acid contains some nitrous acid; when urea is added nitrous acid is destroyed and then the nitric acid, freed from nitrous acid, has no action on mercury.

(ii) *Experiments with mercury (1 g.) and 4 N & 5 N nitric acid (10 c.c.) in presence of sodium nitrite at 25° for a period of 24 hours.*

Table VI.

HNO_3 N	$NaNO_2$ added g.	Mercury taken g.	Free Hg. g.	(Dissolved)-Acid solution			Alkali solution			Nitric oxide (N.T.P.)*	
				$\dot{Hg}$. g.	$\ddot{Hg}$. g.	NO_2' g.	NO_2' c.c. 0. 1N $KMnO_4$	NO_3' c.c. 0. 1N $FeSO_4$	N_2O_3 g.	c.c.	g.
4	0.1000	1.0000	—	0.2718	0.7200	0.0248	not estimated			41.7	0.056
4	0.2000	1.0200	—	0.1698	0.8190	0.0966	„			59.1	0.079
4	0.3000	1.0000	—	0.0800	0.9133	0.1104	„			66.1	0.088
5	0.1000	1.0000	—	—	0.9980	0.0165	„			49.5	0.066
5	0.2000	1.0275	—	—	1.0200	0.0851	„			78.3	0.105
5	0.3000	0.9990	—	—	0.9860	0.1035	„			96.8	0.129

* A large amount of the gas is evolved at the commencement of the experiment.

The above results show that

(*i*) in experiments with 4 N nitric acid, the amount of mercurous mercury diminishes and that of mercuric mercury increases when the amount of sodium nitrite is increased ;

(*ii*) in experiments with 5 N nitric acid all mercury reacts giving mercuric salt ;

(*iii*) the amounts of nitrite in solution and nitric oxide evolved go on increasing as the amount of sodium nitrite is increased.

On comparison of the above results with those given in Tables I and V, it will be seen that the presence of nitrous acid helps not only the dissolution of mercury in nitric acid but also the conversion of mercurous mercury into mercuric mercury. Palit and Dhar (*loc. cit.*) in view of Ray's observation that mercurous nitrite decomposes in presence of water as $2\ HgNO_2 = Hg + Hg(NO_2)_2$, accounted for the increased production of mercuric mercury when sodium nitrite is present by stating that mercuric nitrite would combine with sodium nitrite forming a complex nitrite of the type : $Na_2Hg(NO_2)_4$; consequently in the action of nitric acid on mercury, although mercurous nitrite is the initial product of the reaction, the interaction in presence of sodium nitrite produces hardly any mercurous nitrite. The facts that

(*i*) even in absence of sodium nitrite, mercury interacts with nitric acid giving mercuric salt in solution (Table I, II III & IV),

(*ii*) when sodium nitrite is added to mercury and nitric acid,
  (*a*) sodium nitrite reacts vigorously with nitric acid evolving nitrogen tetroxide and nitric oxide in quantity, and

  (*b*) the amounts of mercuric mercury and nitrite found in the above experiments are not in agreement with the supposed formation of $Na_2Hg(NO_2)_4$.

however, show that the explanation advanced by Palit and Dhar is not tenable. On the other hand, it seems highly probable that the addition of sodium nitrite increases the amount of nitrous acid which in turn accelerates the oxidation of mercurous mercury.

Conversion of (a) mercurous mercury into mercuric mercury by the action of nitric acid and (b) mercuric mercury into mercurous mercury by the action of mercury.

(*a*) *Conversion of mercurous mercury into mercuric mercury : the action of nitric acid on mercurous nitrite in absence and presence of urea.*

From the foregoing experiments it appears that the production of mercuric mercury in the action of nitric acid on mercury is in all probability due to the oxidation of mercurous mercury by the action of nitrous acid. If the production of mercuric mercury, on the other hand, were due to either (*i*) the decomposition of mercurous nitrite according to Ray's equation or (*ii*) the oxidation of mercurous mercury by means of nitric acid alone, one would expect the formation of mercuric mercury in (*i*) when mercurous nitrite is treated with nitric acid of low concentrations and in (*ii*) when mercurous salt is treated with nitric acid of high concentrations in absence of nitrous acid. Experiments were, therefore, conducted with mercurous nitrite and nitric acid (10 c.c.) of different concentrations in absence and presence of urea. The results of these experiments are given below in Table VII.

Experiments with mercurous nitrite and nitric acid (10 c.c.) in absence and presence of urea at 25° for a period of 24 hours.

Table VII.

				(Dissolved)-Acid solution			Alkali solution			Gas (N.T.P)	
HNO_3 N	Urea added g.	$HgNO_2$ taken g.	Free Hg g.	$Hg^{\cdot}$ g.	$Hg^{\cdot\cdot}$ g.	NO_2' g.	NO_2' c.c. 0.1N $KMnO_4$	NO_3' c.c. 0.1N $FeSO_4$	N_2O_3 g.	c.c.	g.
2	—	0.1045	—	0.0810	—	not estimated				4.8	0.0064*
2	—	0.2035	—	0.1620	—	„				10.0	0.0135*
3	—	0.1000	—	0.0700	0.0120	„				5.0	0.0067*
3	—	0.2000	—	0.1320	0 0300	„				11.1	0.0147*
3	0.200	0.2000	—	0.1600	—	„				25.8	0.0525**
4	—	0.1025	—	0.0700	0.0100	„				2.0	0.0028*
4	—	0.2000	—	0.1100	0.0500	„				5.5	0.0073*
4	0.200	0.2000	—	0.1585	—	„				25.0	0.0312**
5	—	0.2000	—	0.0120	0.1500	„				11 6	0.0154*
5	0.200	0.2000	—	0.1500	—	„				26.0	0.0325**

The above results show that

(*i*) no free mercury is found to separate in these experiments ;

(*ii*) in absence of urea the conversion of mercurous mercury to mercuric mercury is not observed in experiments with 2 N nitric acid, but is observed to some extent in experiments with 3 N and 4 N nitric acid, and completely in experiments with 5 N nitric acid ; further with the increase in the amount of mercurous nitrite the production of mercuric mercury increases in experiments with 3 N and 4 N nitric acid ;

(*iii*) in presence of urea no formation of mercuric mercury is observed in experiments with 3 N. 4 N and 5 N nitric acid.

From the above observations it may be concluded that (1) the production of mercuric mercury from the decomposition of mercurous nitrite according to Ray's equation is not observed in nitric acid solution and (2) nitric acid when free from nitrous acid does not oxidise mercurous mercury. Thus if mercuric mercury is produced in the action of nitric acid on mercury, it is obtained from the oxidation of mercurous mercury by the action of nitrous acid either alone or in presence of nitric acid.

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* Nitric oxide. ** Nitrogen.

(*b*) *Conversion of mercuric mercury into mercurous mercury : the action of mercury on mercuric nitrate.*

From the experimental results given in Tables I, II and III, it will be seen that the production of mercurous mercury is great and of mercuric mercury low so long as free mercury is present. One may infer from this observation that the initial product of the interaction between mercury and nitric acid may be mercuric salt (rather than mercurous salt) which on reduction with free mercury in the secondary stage may give rise to mercurous salt. The fact that in absence of mercury the oxidation of mercurous mercury to mercuric mercury proceeds continuously along with the formation of nitrite and nitric oxide when the interaction is allowed to proceed for a long time or at high temperature (*vide* Tables II and III) shows, on the other hand, that this view is not probable. In order to get further information, experiments were conducted with mercury (1 g.) and varying amounts of mercuric nitrate dissolved in 1 N nitric acid (10 c.c.). The results of these experiments are given in Table VIII.

Experiments with mercury (1 g.) and mercuric nitrate dissolved in 1 N nitric acid (10 c.c.) at 25° for a period of 24 hours.

Table VIII.

$Hg(NO_3)_2$ taken g.	Mercury taken g.	Free Hg g.	(Dissolved)-Acid solution			Alkali solution			Gas. (N.T.P.)	
			$Hg^{\cdot}$ g.	$Hg^{\cdot\cdot}$ g.	NO_2' g.	NO_2' c. c. 0.1N $KMnO_4$	NO_3' c. c. 0.1N $FeSO_4$	N_2O_3 g.	c.c.	g.
0.0500	1·0020	0·9835	0·0135	0·0200	—	—	—	—	—	—
0·1000	1·0050	0·9800	0·0210	0·0520	—	—	—	—	—	—
0·2475	1·0055	0·9280	0·1402	0·0970	—	—	—	—	—	—
0·4980	1·0008	0·8775	0·2548	0·1950	—	—	—	—	—	—
1·0000	1·0020	0·7685	0·4217	0·4600	—	—	—	—	—	—
1·5000	0·9990	0·7050	0·5690	0·7158	—	—	—	—	—	—

The above results show that

(*i*) mercury reduces mercuric mercury to mercurous mercury in all experiments;

(*ii*) the conversion of mercuric mercury to mercurous mercury *is approximately proportional to the amount of mercuric* nitrate used;

(*iii*) the conversion is not complete even when the amount of mercuric nitrate used in the experiment is very small.

The fact that in the above experiments all mercuric mercury is not reduced to mercurous state even when the amount of mercuric nitrate used is very small, whereas in experiments given in Table II the interaction leads to the production of mercurous mercury alone in the initial stage, shows that mercurous salt, and not mercuric salt, is the initial product of the interaction between mercury and nitric acid.

SUMMARY OF RESULTS AND CONCLUSION

The results of all the above experiments taken together show that nitric acid in a pure state i.e., when free from nitrous acid has no action on mercury in agreement with the observations of Million (*loc. cit.*), Divers (*loc. cit.*) and Veley (*loc. cit.*). Merck's extra pure nitric acid which evidently contains some nitrous acid interacts with mercury giving mercurous and mercuric mercury and nitrite in solution together with the evolution of nitric oxide and some nitrogen tetroxide, and the proportions of each of these vary depending upon the concentration of nitric acid used, the time of interaction, the temperature of the experiment and the mass of mercury taken.

The present results, further, show that the interaction proceeds mainly in two stages: (1) the dissolution of mercury to mercurous mercury, and (2) the oxidation of mercurous mercury to mercuric mercury, accompanied with the production of nitrite and nitric oxide. Both these stages are accelerated by increasing the amount of nitrous acid in nitric acid and inhibited when the nitrous acid is eliminated by the addition of urea to nitric acid. Moreover, by taking a large quantity of mercury it is possible to increase the production of mercurous mercury and nitrite so as to lead to the separation of yellow crystals of mercurous nitrite, and conversely by reducing the quantity of mercury it is possible to decrease the production of mercurous mercury and increase that of mercuric mercury. Further, when the concentration of nitric acid is high, nitrogen tetroxide is also evolved.

On the whole, it may be concluded that the interaction between mercury and nitric acid mainly depends upon the presence of nitrous acid in nitric acid. Since neither hydrogen nor any hydrogen compound of nitrogen is ever produced in the interaction, it seems highly probable that the process involved in the interaction between mercury and nitric acid consists of oxidation of mercury to mercurous and mercuric mercury, and reduction of nitric acid to nitrous acid and oxides of nitrogen. Further work elucidating the behaviour of nitrous acid in the various stages of the interaction is in progress.

Our thanks are due to Prof. D. D. Kanga, Mr. C. L. Mankodi and Dr. K. S. Nargund for interest in the work.

One of us (M. S. S.) acknowledges his indebtedness to the University of Bombay for a research grant.

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STUDY OF A REACTION BETWEEN AQUEOUS SOLUTIONS OF MERCURIC CHLORIDE AND DISODIUM HYDROGEN PHOSPHATE

By

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Rose (*Handbuch der analytischen chemi.*, 1851, 1, 382) obtained no immediate precipitate on mixing solutions of mercuric chloride and sodium phosphate but a reddish precipitate after a long time. He also noticed that the precipitate can be obtained quickly on heating. Liebig (Liebig's *Ann.*, 1853, 85, 307) observed no turbidity on mixing the above solutions but obtained a small quantity of a red precipitate after the mixture had stood for a long time. This observation remained in oblivion for nearly thirty-eight years when Haack (*Liebig's Ann.*, 1891, 262, 188) while investigating arsenates and phosphates of mercury found, on mixing dilute or concentrated solutions of mercuric chloride and sodium phosphate, that yellow turbidity and then a yellow precipitate appear which change to a reddish brown colour after a time with the complete disappearance of the yellow colour. This interesting reaction has not been studied by any other investigator. A study of this reaction was therefore undertaken and the results of the investigation under different conditions of temperature and concentration as well as of the isolation of the yellow intermediate substance are described in this paper.

EXPERIMENTAL

Merck's G. R. Mercuric chloride (38·13 grams) and sodium phosphate $Na_2HPO_4.12H_2O$ (200·02 grams) were each dissolved in water (500 c.c.) at 30°C and only the sodium phosphate solution was diluted so as to be (i) 0·2 (ii) 0·3 (iii) 0·4 (iv) 0·5 (v) 0·6 (vi) 0·7 (vii) 0·8 and (viii) 0·9 of the original concentration which was 2·235N with respect to its sodium content. It was found by trial that a solution of sodium phosphate diluted to one tenth of the original concentration gave, on mixing with the solution of mercuric chloride, a yellow turbidity which yielded small quantity of a reddish brown powder on heating. Since the quantity of the precipitate thus obtained was very small solutions of sodium phosphate less dilute than one fifth of the original strength were not used.

The method adopted for the reactions was to take 60 c.c. of each of the reacting solutions in wide-mouthed test tubes and then to place them in an air thermostat maintained at 30°C or 40°C with a variation of ±0·1°C by means of a toluene regulator which controlled an electric relay and a heater. After the test tubes had stood in the thermostat for about half an hour, during which time the solutions attained the temperature of the thermostat, the solution of sodium phosphate was added to that of mercuric chloride, the test tube corked and then inverted upside down six times. This method of mixing was used in all the experiments. In order to carry out the reaction at 90°C the two test tubes were heated to the required temperature in a water bath and the same method of mixing as used before was followed. It was found that a yellow turbidity appeared immediately on mixing the two solutions and developed into a yellow precipitate at the bottom of the test tube. After a time a colour change set in, which finally resulted in the whole of the yellow precipitate being converted into a reddish brown substance and the supernatant liquid becoming clear. This is in accord with the observations of Haack (*loc. cit.*). The approximate time required for the complete change of colour since mixing of the two solutions was noted for reactions proceeding at 30°C and 40°C. For reactions at 90°C the time required for a complete change of colour was short and nearly the same in all the experiments. The amount of the precipitate obtained in each experiment was also noted.

After the complete change of colour had taken place the reddish-brown precipitate was filtered, washed with distilled water (250 c.c.), dried at room temperature (about 28°C) and finally treated with anhydrous ether in which mercuric chloride dissolves but not the compound. It was then allowed to dry and powdered in an agate mortar.

The percentage of mercury in each sample was determined by the gravimetric method which was tested by the analysis of pure mercuric chloride and found to give results with an error not exceeding 0·3 per cent. For this purpose a weighed quantity of the sample was dissolved in dilute hydrochloric acid and mercury in it was estimated as mercuric sulphide after precipitation by means of freshly prepared ammonium sulphide. It was filtered through a gooch crucible, washed in the usual manner, and dried at 110°C.

A few samples were analysed for their chloride content. This was done by dissolving a weighed sample in a known volume of standardised dilute hydrochloric acid. From this solution mercury was first precipitated as sulphide as before, filtered off and the chloride estimated in the filtrate volumetrically after boiling off the excess of sulphuretted hydrogen by means of standard silver nitrate using potassium chromate as indicator.

The hydrogen ion concentration of the solutions of sodium phosphate used in this investigation was also determined by means of the glass electrode method described by Mehta (*J. Univ. Bom.*, 1936, 5(2), 77).

The results obtained are given in tables I to III in which the following symbols are used :

N = normality of sodium phosphate in terms of its sodium content ;

T = time in minutes since mixing of the solutions for a complete change of colour ;

W = weight of the reddish-brown precipitate in grams ;

P = per cent of mercury in the sample.

TABLE I

Temperature = 30°C

N	pH	T	W	P
0·4460	8·92	41	0·8155	84·48
0·6705	8·88	33	1·012	86·18
0·8940	8·85	21	0·7787	85·74
1·1175	8·80	54	1·113	85·07
1·3410	8·75	40	1·3669	84·24
1·5645	8·708	30	1·585	84·86
1·7880	8·69	25	1·398	85·90
2·0115	8·66	27	1·3871	84·15
2·2350	8·655	24	1·7867	84·94

TABLE II

Temperature = 40°C

N	T	W	P
0.4460	15	0.8803	85.33
0.6705	75	0.971	84.55
1.3410	13	1.2722	85.27
1.788	23	1.2692	85.14
2.2350	5	0.4885	85.00

TABLE III

Temperature = 90°C

N	T	W	P
0·4460	Varies between 2 and 5 minutes	0·6489	86·36
0·6705		0·716	86·36
0·8940		1·31	87·28
1·1175		1·3116	87·60
1·3410		1·4811	87·10
1·5645		1·3107	87·43
1·7880		1·6337	87·72
2·0115		1·5445	87·98
2·235		1·2625	87·24

Tables I to III show that the percentage of mercury in each of the samples varies only to a small extent with a change in the concentration of sodium phosphate solution. They show further that a variation in pH of the solution of sodium phosphate within narrow limits has no appreciable effect on the composition of the precipitate. But when the effect of temperature is examined it is found that a change of temperature to 90° affects the percentage of mercury in the compound.

On an examination of the above tables it is found that at 30° and 40°C the percentage of mercury in the different samples agrees fairly well with that corresponding to the formula $2HgO. HgCl_2$. At 30°C the percentage of mercury in the various samples deviates from the theoretical value (85·39) between 0·9014 and 1·603 per cent while at 40°C it deviates between 0·09365 and 1·009 per cent. The percentage of mercury in the samples obtained at 90°C agrees with the formula $3HgO.HgCl_2$: the deviations from the theoretical value (87·1) lie between 0·8496 and 1·010 per cent. It appears therefore that the compound $2HgO.HgCl_2$ is formed at 30° and 40°C and that $3HgO.HgCl_2$ is formed at 90°C. These conclusions are in agreement with the test estimations of chloride which were 10·90 and 7·63 per cent respectively.

The time required for the change of colour as well as the quantities of the samples obtained do not show a regular gradation.

Attempts were made to isolate the yellow substance with a view to get an insight into the mechanism of the reaction. After several trials to lengthen the time of colour change by the addition of glycerol and mannitol as well as by lowering the temperature it was found that the best procedure was to remove the yellow compound from the mother liquor by filtering it at the water pump soon after its formation. The yield thus obtained was, however, very poor : the quantity obtained from one reaction being only about 0·05 gram. The samples thus obtained were perfectly stable and did not change in colour on keeping.

A sample of this substance was dissolved in concentrated nitric acid and on a quantitative analysis was found to contain Hg = 81·75, P = 1·48 and Cl = 5·707 per cent. When dissolved in dilute nitric acid it gave a small quantity of a white residue which from two different samples was 23·51 and 11·32 per cent respectively. From these results it appears that the yellow substance is neither pure mercuric oxide nor mercury phosphate but probably a mixture of the latter with an oxychloride of mercury the proportions of which vary with experimental conditions.

SUMMARY

1. Solutions of mercuric chloride and disodium hydrogen phosphate react to give $2HgO.\ HgCl_2$ at 30° and 40°C and $3HgO.\ HgCl_2$ at 90°C.

2. A change in the pH of the solutions of sodium phosphate between 8·655 and 8·92 has no appreciable effect on the composition of the precipitate.

3. A yellow substance, formed soon after mixing the two solutions, has been isolated and it is shown that it is neither pure mercuric oxide nor mercury phosphate but probably a mixture of the latter with an oxychloride of mercury.

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SOME REACTIONS OF OXANILIDE-DI-IMIDOCHLORIDE (DIPHENYL-OXAL-IMIDOCHLORIDE)

By

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The present research is a part of the comprehensive investigation of the reactions of the little studied aliphatic di-imidochloride-oxanilide-di-imidochloride (Wallach and Pirath, *Ber.*, 1880, *13*, 527; Bauer, *Ber.*, 1907, *40*, 2650; Reitenstein and Breuning, *J. Pr. Chem.* 1911 (ii) *83*, 97).

Oxanilide-di-imidochloride, unlike imidochlorides derived from aliphatic acids, is highly stable and it was thought of interest to study its various reactions with the ultimate object of comparing them with the reactions of imido-chlorides derived from aromatic acids.

In this paper reactions of oxanilide-di-imidochloride with aniline, sodium ethylate and sodium phenate have been studied. The imidochloride yields with aniline the diamidine, tetra-phenyl-oxalamidine, the condensation being effected by Shah's modified method (*J. Ind. Inst.*, *Sc.* 1925, *7*, 219). *Bauer* (*loc. cit.*) obtained this diamidine by a very lengthy procedure. The diamidine forms a di-hydrochloride. The action of sodium ethylate produces di-ethyl-di-(phenyl-imino)-oxalate obtained as a crystalline solid, and with sodium phenate di-phenyl-di-(phenyl-imino)-oxalate is obtained.

By the action of EtI and silver oxide on oxanilide, Lander (*J.* 1901, 700) obtained di-ethyl-di-(phenyl-imino)-oxalate in the form of a dark brown liquid b.p. 205°/12 mm. It is interesting to note that by the action of alcoholic KOH on di-o-tolyl-oxal-imidochloride, Bauer (*loc. cit.*) obtained ethyl-o-tolyl-imino-o-tolyl-oxamate as well as di-ethyl-di-(o-tolyl-imino)-oxalate.

EXPERIMENTAL

Oxanilide-di-imidochloride (*di-phenyl-oxal-imido-chloride*).

Oxanilide-di-imidochloride was prepared according to the method of Bauer (*Ber.* 1907, 40, 2653) from oxanilide (Kahlbaum's chemically pure) and PCl_5 in 70-75% yield (yield obtained by Bauer 70% theory) m.p. 113-115°. (m.p. given by Bauer, 115°).

Tetra-phenyl oxalamidine (Bauer, *Ber.*, 1907, *40*, 2655).

It was prepared according to the method of Shah (*J. Ind. Inst. Sc.*, 1925, 7, 215).

Mixture of oxanilide-di-imidochloride (5g. : 1 mol.), freshly distilled di-ethyl aniline (16 g. : 6 mols.) and aniline (5 g. : 3 mols.)

was heated on water bath for 1 hour, allowed to stand overnight, and next day treated with hydrochloric acid (1 : 1) when the dihydro-chloride separated ; on trituration with pyridine it yielded tetra-phenyl-oxalamidine. The di-amidine crystallizes in light yellow prismatic needles m.p. 156-158° (m.p. obtained by Bauer 153°); yield 6 g. (86%). (Found : C, 80·2% ; H, 5·7% ; N, 14·7% ; $C_{26}H_{22}N_4$ requires C, 80% ; H, 5·6% ; N, 14·4%).

Tetra-phenyl-oxalamidine forms the *di-hydrochloride* when treated with concentrated hydrochloric acid in glacial acetic acid solution ; it is a pale yellow crystalline solid m.p. 242°. (Found : Cl, 15·0% ; $C_{20}H_{24}N_4Cl_2$ requires Cl, 15·3%).

(*Di-ethyl-di-phenyl-imino*) *-oxalate* (c.f. Lander J. 1901, 700).

Mixture of oxanilide-di-imidochloride (1 mol.) and sodium ethylate prepared from sodium (2 atoms) and absolute alcohol was refluxed in anhydrous toluene for 4 hours, treated with water to remove NaCl formed, and extracted with ether ; ether and toluene were distilled, and the residue allowed to stand for crystallization ; di-ethyl-di- (phenyl-imino) -oxalate crystallized from light petroleum in transparent plates m.p. 42° [Lander (*loc. cit.*) gives b.p. 205°/12 mm.] (Found : C, 72·9% ; H, 6·8% ; N, 9·6% ; $C_{18}H_{20}O_2N_2$ requires C, 72·9% ; H, 6·8% ; N, 9·5%).

It is easily soluble in light petroleum, benzene and toluene ; it is difficultly soluble in other organic solvents.

Di-phenyl-di- (phenyl-imino) -oxalate.

Mixture of oxanilide-di-imidochloride (10 g. : 1 mol.) and sodium phenate prepared from sodium (1·66 g. : 2 atoms), phenol (6·8 g. : 2 mols.) and absolute alcohol was refluxed in anhydrous ether for four hours and evaporated to dryness ; the product was treated with water when di-phenyl-di- (phenyl-imino) -oxalate was obtained in the form of a pasty mass which solidified after some time ; it crystallizes from petroleum ether in white tiny needles m.p. 130-132° ; yield 3 g. (21%).

(Found C, 79·5% ; H, 5·4% ; N, 7·4%. $C_{26}H_{20}O_2N_2$ requires C, 79·6% ; H, 5·1% ; N, 7·1%).

Di-phenyl-di-(phenyl-imino) -oxalate is easily soluble in light petroleum, benzene and toluene ; it is difficultly soluble in other organic solvents.

One of the authors (V. R. H.) is grateful to the University of Bombay for the award of a research grant for the above investigation.

The authors thank Dr. T. S. Wheeler for his keen interest in the work.

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THE ACTION OF THIONYL CHLORIDE AND SULPHUR DI-CHLORIDE ON METHYL SALICYLATE

By

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Hirve, Jadhav and Chakradeo (*J. Univ. Bom.*, 1933 Sept. 128-131, *J. Ind. Chem. Soc.* 1934, 551,-554 *J. Amer. Chem. Soc.* 1935, 101-103) studied the action of thionyl chloride on the esters of salicylic acid in the presence of copper. They required copper in molecular quantities and not in small quantities as they should have if it were acting as a catalyser. Hence they explained the reaction by presuming that copper actually entered into reaction with thionyl chloride and thereby several products such as sulphur dichloride, sulphur mono-chloride, sulphur dioxide etc. were formed. The former two then reacted with the esters of salicylic acid as under :

$$2C_6H_4OH\ COOR + S.Cl_2 = (C_6H_3OH\ COOR)_2S + 2HCl \quad (1)$$

$$2C_6H_4OH\ COOR + S_2Cl_2 = (C_6H_3OH\ COOR)_2S + S + 2HCl \quad (2)$$

where

$R = CH_3,\ C_2H_5,\ C_6H_5$ etc.,

In search of real catalysers for the reaction between thionyl chloride and the esters of salicylic acid which do not react in the absence of catalysers, several metals or their chlorides were tried and it was found that only zinc dust, iron dust and the chlorides of zinc, iron, bismuth and antimony worked satisfactorily, about 0·2 gram being sufficient for 10 grams of the ester.

The most suitable proportion for the reaction was two mols of thionyl chloride for every two mols of the ester though it was found that out of the two molecules of thionyl chloride, only one was actually used up, the other one was probably swept away by the hydrochloric acid gas evolved in the reaction. Roughly quantitative experiments show that a part of the thionyl chloride is swept away. The reaction took place with copious evolution of hydrochloride acid gas and was over in six hours at 40°-50°C. The resulting products were identical with the thio-ethers obtained by Hirve, Jadhav and Chakradeo (*loc. cit.*). Generally no sulphur was found to be precipitated in the course of the reaction. As no sulphur is precipitated, formation of sulphur mono-chloride seems to be improbable as the equation (2) (wide *supra*) demands the precipitation of sulphur. As the metals or their chlorides are required in very small quantities, the question of their having entered into reaction with thionyl chloride, does not arise.

No satisfactory mechanism of the formation of the sulphides can be advanced at this stage. The view that sulphur dichloride is formed in the first stage was first entertained, and appeared to be supported by the observations that sulphur dichloride in the presence of the catalysers also gives the sulphides. However as no experimental evidence for this view could be obtained this view of the mechanism is no longer tenable. An experimental fact which may have some bearing on the question is that sulphuryl chloride does not appear to be formed in the reaction.

EXPERIMENTAL

Effect of different catalysers.

Every time 10 grams of methyl salicylate and 8 grams thionyl chloride (or 3·5 grams of sulphur dichloride) were taken in a test tube which had a cork with a drawn out bent tube on it. As the tube was drawn out, no moisture could come in. The yields with the different catalysers were as under :

Catalyser	*with sulphur dichloride*	*with thionyl chloride*
$BiCl_3$	66·3 per cent.	73 per cent
$ZnCl_2$	58 ,,	69 ,,
$SnCl_2$	45 ,,	59 ,,
$SbCl_3$	43·6 ,,	56 ,,
$FeCl_3$	42 ,,	50 ,,

These results show that the catalytic effect of the different catalysers is of the same order whether the reaction is with sulphur dichloride or with thionyl chloride.

In the case of ethyl salicylate and salol the reaction was not quantitatively followed with all the catalysers mentioned above, but with zinc chloride alone it was found that the yields varied between 32 and 42 per cent. However it was observed qualitatively that the reaction did go on with the rest of the catalysers as well.

Sulphuryl chloride was not detected in the reaction mixtures after the reaction was over, as well as in the gases which were evolved during the reaction.

Every time 10 grams of methyl salicylate and 8 grams of thionyl chloride were allowed to react in the presence of a catalyser i.e. zinc chloride, bismuth chloride etc. In the case of the reaction mixture, the same was extracted with water after the reaction was over and in the case of the gases which evolved, these were allowed to bubble through a series of flasks filled with alkali solution. The solutions so obtained, were not found to contain any sulphate as they should, if sulphuryl chloride were formed i.e., $SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$.

In the end we take this opportunity to thank the University of Bombay for a grant which enabled us to carry out this piece of work. We also record our thanks to Dr. Wheeler of the Royal Institute of Science, Bombay, for having lent or given us certain chemicals whenever we asked for the same.

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THE CONDENSATION OF ARYLAMINES WITH THE CYANOHYDRINE OF r-CAMPHOR AND 3-METHYLCYCLOPENTANONE

By

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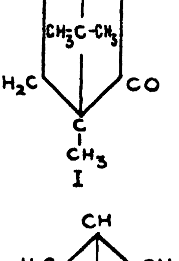
In continuation of the work published from these laboratories[1] on the condensation of arylamines with the cyanohydrins of cyclic-ketones, it was desirable to extend this investigation to camphor (I) and 3-methylcyclopentanone. (II) Camphor bears a striking pictorial resemblance to O-methylcyclo-hexanone (III), and as we have already studied the condensation of O-methylcyclohexanone-cyanohydrin with aromatic amines, and obtained evidence of cis-trans isomers, it was just possible that a similar type of results might be obtained by preparing 1-cyano-1-arylaminocamphane (IV), (R = aryl).

Crystalline products were obtained by condensing the camphor-cyanohydrin with aniline, p-bromaniline, p-toluidine, α-and β-naphthylamines, but as each derivative was obtained in only one form, there was no possibility of any type of isomerism in such cases. O-



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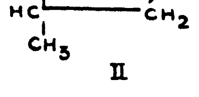

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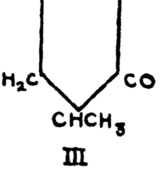

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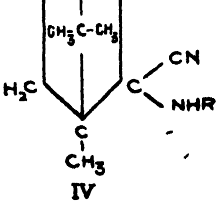
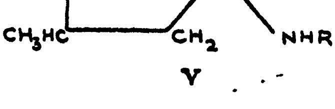


IV



V

and m-toluidines gave viscous gums which did not solidify even after six months; neither did they yield any solid carbamyl derivatives which were readily obtainable from the solid cyanoarylaminocamphanes by keeping them in contact with concentrated sulphuric acid.

The two isomeric forms of arylaminocyano-methylcyclohexanes obtained by one of us[1] may be the cis-transforms of the uniplanar cyclohexane ring, or they may be the stable derivatives of the two multiplanar forms of the six-membered ring. To gain further information on this point, the condensation of the cyanohydrin of 3-methylcyclopentanone with arylamines, which was expected to lead to the formation of a pair of cis-trans isomers, derived from the uniplanar five-membered ring, was examined, but only one form of 1-arylamino-1-cyano-3-methylcyclopentanes (V, where R = aryl) was isolated. Aniline, p-bromaniline, p-toluidine,α-and β-naphthylamines gave solid condensation products, while O-and m-toluidines gave gummy products which were readily convertible into solid carbamyl derivatives. Thus we have not been able to realise the evidence for the cis-trans type of isomerism in any case.

EXPERIMENTAL

1-anilino-1-cyanocamphane. (IV, R = C_6H_5).

A solution of potassium cyanide (5g) in water (10 c.c.) was added to a mixture of r-camphor (11·7g), and aniline (7·2g) in glacial acetic acid (30 c.c.) and kept overnight. There separated an oil which solidified on cooling in a freezing mixture, and the solid crystallised from benzene in lustrous plates m.p. 152°. The mother-liquor gave further quantity of the same product contaminated with camphor, which was removed by washing with petroleum ether. (Yield almost quantitative).

(Found C, 79·9; H, 8·7; $C_{17}H_{22}N_2$ requires C, 80·3; H, 8·7 per cent).

The Carbamyl derivative, obtained by keeping a solution of the nitrile in concentrated sulphuric acid, crystallised from benzene in prisms m.p. 160°. (Found C, 75·0; H, 8·8; $C_{17}H_{24}N_2O$ requires C, 75·0; H, 8·8 per cent).

1-p-bromanilino-1-cyanocamphane, which was similarly prepared from p-bromaniline (8·6g) camphor (7·5g), KCN (3·5g in 10 c.c. water) and glacial acetic acid (20 c.c.) crystallised from benzene in white prisms m.p. 162°.

(Found Br, 23·92; $C_{17}H_{21}N_2$ Br requires Br, 24·02 per cent). *The amide,* crystallised from benzene in small needles m.p. 189°. (Found Br, 22·7; $C_{17}H_{23}N_2O$ Br requires Br, 22·8 per cent). 1-*p-toluidino*-1-*cyanocamphane,* was prepared from p-toluidine (7g), camphor (7·5g.), KCN (3·5g. in 10 cc. water) and glacial acetic acid (20 cc.), and crystallised from benzene in white needles m.p. 143°.

(Found C, 80·3 ; H, 9·1 : $C_{18}H_{24}N_2$ requires C, 80·6 ; H, 9·0 per cent). The amide crystallised from alcohol in fine scales m.p. 190°.

(Found C, 75·4 ; H, 9·2 : $C_{18}H_{26}N_2O$ requires C, 75·5 ; H, 9·1 per cent). 1-*β-Naphthylamino*-1-*cyanocamphane*, which was prepared from *β*-naphthylamine (7g.), camphor (7·5 g.), potassium cyanide (3·5 g. in 10 cc. water) and glacial acetic acid (30 cc.) crystallised from benzene in white needles m.p. 165°.

(Found C, 82·6 ; H, 8·1 : $C_{21}H_{24}N_2$ requires C, 82·9 ; H, 7·9 per cent). *The amide*, crystallised from benzene in scales m.p. 182°.

(Found C, 78·2 ; H, 8·1 : $C_{21}H_{26}ON_2$ requires C, 78·3 ; H, 8·07 per cent.). 1-*α-naphthylamino*-1-*cyanocamphane* could not be obtained in a solid form.

Its amide crystallised from hexane in short needles m.p. 112°.

(Found C, 78·1 ; H, 8·0 ; $C_{21}H_{26}ON_2$ requires C, 78·3 ; H, 8·07 per cent.).

Condensation of 3-*methylcyclopentanone-cynohydrin* with amines.

3-methylcyclopentanone was prepared by the method of Desai.[2] Its condensation with aniline and KCN has already been described by Desai, Hunter and Mehdi Hussain.[1]

1-p-*toluidino-l-cyano*-3-*methylcyclopentane* (V, where R=p-tolyl).

A solution of KCN (7 g.) in water (30 cc.) was added to a mixture of p-toluidine (11 g.), 3-methylcyclopentanone (10 g.) and glacial acetic acid (30 cc.) and kept aside for 24 hours. The solid that separated out was filtered off, and on diluting the mother-liquor with water, a further quantity of the solid was obtained (Yield almost quantitative). The crude product m.p. 62-65° was crystallised from petrol when thick plates m.p. 66-67° were obtained.

(Found C, 78·3 ; H, 8·5 : $C_{14}H_{18}N_2$ requires C, 78·5 ; H, 8·4 per cent.).

The *amide*, was obtained by keeping the nitrile (1 g.) in solution with concentrated sulphuric acid (5 cc.) overnight, pouring the solution in water, and making the aqueous solution alkaline with concentrated ammonia. The solid crystallised from dilute alcohol in lustrous plates m.p. 126°.

(Found C, 72·5 ; H, 8·7 ; $C_{14}H_{20}ON_2$ requires C, 72·4 ; H, 8·6 per cent.)

1-p-*bromanilino*-1-*cyano*-3-*methylcyclopentane*, was prepared from p-bromaniline 8·6 g.), the ketone (5 g.), and KCN (3·5 g.) in water

(10 cc.) and glacial acetic acid (20 cc.). It crystallised from petrol in light, silky needles m.p. 69-70°.

Found Br, 28·8 ; $C_{18}H_{15}N_2$ Br requires Br, 28·67 per cent.)

The amide, crystallised from alcohol in lustrous plates m.p. 163-164°. (Found Br. 27·1 ; $C_{18}H_{17}ON_2$ Br. requires Br. 26·9 per cent.) 1-*α-naphthylamino*-1-*cyano*-3-*methylcyclopentane,* was prepared from α-naphthylamine (7·7 g.)— the ketone (5 g.), KCN (3·5 g.) water. (10 cc.) and glacial acetic acid (20 cc.). The product crystallised from petrol in needles m.p. 94°.

(Found C, 81·3 ; H, 7·4 : $C_{17}H_{18}N_2$ requires C, 81·6 ; H, 7·2 per cent.).

1 - *β* - *naphthylamino*-1-*cyano*-3-*methylcyclopentane,* crystallised from petrol in thick plates m.p. 89°. (Found C, 81·4 ; H, 7·1 : $C_{17}H_{18}N_2$ requires C, 81·6 ; H, 7·2 per cent.)

The *amide,* was obtained from alcohol as a microcrystalline solid m.p. 253°.

(Found C, 75·9 ; H, 7·5 : C_{17} $H_{20}ON_2$ requires C, 76·1 ; H, 7·46 per cent.)

1-*o-toluidino*-1-*cyano*-3-*methylcyclopentane,* could not be obtained in a solid form. Its *amide* crystallised from dilute alcohol in small needles m.p. 89°.

(Found C, 72·1 ; H, 8·5 ; $C_{14}H_{20}ON_2$ requires C, 72·4 ; H, 8·6 per cent.).

The *amide* of 1-*m-toluidino*-1-*cyano*-3-*methylcyclopentane* crystallised from dilute alcohol in needles m.p. 85°.

(Found C, 72·3 ; H, 8·8 ; $C_{14}H_{20}ON_2$ requires C, 72·4 ; H, 8·6 per cent.).

We have great pleasure in expressing our thanks to Dr. R. F. Hunter for his kind interest in this work.

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HETEROCYCLIC COMPOUNDS PART VI. COUMARINS FROM ETHYL-β-CHLOROPROPYLACETOACETATE AND THE MERCURATION OF COUMARINS FROM ETHYLCYCLOHEXANONE-2-CARBOXYLATE

By

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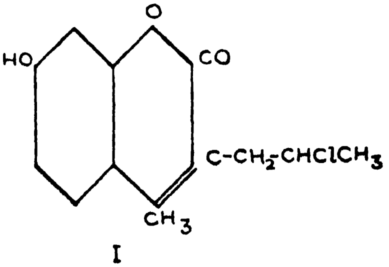
By condensing ethyl allyl-acetoacetate with resorcinol in the presence of hydrogen chloride Naik, Desai and Desai[1] observed the formation of a chlorocoumarin ; its stability in the presence of water precluded the possibility of an oxonium salt formation from 7-hydroxy-4-methyl-3-allyl-coumarin while the addition of the halogen acid to the double bond at the 3 : 4 position was far remote in the light of the observation of Ghosh.[2] Therefore, the resulting compound was formulated as 7-hydroxy-4methyl-3-β-chloropropylcoumarin (I), arising by the addition of hydrogen chloride to 7-hydroxy-4-methyl-3-allylcoumarin at the allyl group.



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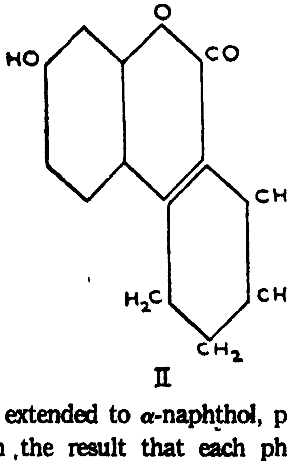

II

These observations have now been extended to α-naphthol, pyrogallol, orcinol, and phloroglucinol with the result that each phenol gave a similar type of coumarin. Treatment with alcoholic sodium ethoxide converted the β-chloropropyl group into the allyl radical.

The mercuration of coumarins containing the cyclopenteno group substituted in the 3 : 4 positions of the coumarin ring has already been described by the author.[3] To ascertain the effect of the cyclohexeno group in these positions, on the course of this reaction, coumarins have been prepared by condensing ethyl cyclohexanone-2-carboxylate with resorcinol, phloroglucinol, orcinol, and 4-ethylresorcinol with the formation of 7-hydroxyclohexeno (1′ : 2′ : 4 : 3)—coumarin (II), and 5 :7-dihydroxy, 7-methyl-5-hydroxy—, and 6-ethyl-7-hydroxy-cyclo-hexeno (1′ : 2′ : 4 : 3)—coumarins. The coumarin (II) which has already been prepared by Dieckmann[4] was mercurated together with its two congeners by the method already described in Part I of this series,[3] with the formation of triacetoxymercuri derivatives in each case. The acetoxymercuri groups must have occupied 6 : 8 positions as they are free, but the actual position of the third group is unknown, and we are busy closely investigating this point.

Following the observations of Goswami,[5] we tried the preparation of benzopyrylium salts from these coumarins. Red or blue coloured solids, soluble in concentrated hydrochloric acid were obtained, but the experiments were discontinued as ferrichlorides could not be obtained in a pure condition.

EXPERIMENTAL

7 : 8 *dihydroxy-4-methyl-3-β-chloropropyl-coumarin.*

Dry hydrogen chloride was passed into a cold mixture of allylacetoacetic ester (3·4 g.), pyrogallol (2·5 g.) and glacial acetic acid (15 cc.) for one hour, and kept overnight. The solid which separated out slowly on diluting the mixture with water was collected, and crystallised from dilute alcohol or dilute acetic acid in colourless needles m.p. 193-194°. (Yield 2·5 g.). (Found Cl, 13·0 ; $C_{13}H_5O_4$ Cl requires Cl, 13·2 per cent.).

Conversion into 7 : 8 *dihydroxy-4-methyl-3-allylcoumarin.*

The solution of the above coumarin (0·5 g.) in sodium ethoxide (1 g.) Na ; (20 cc.) absolute alcohol was refluxed on a water-bath for two hours. The residue left after removing alcohol was dissolved in water, and the filtered solution was cautiously acidified with dilute HCl. The solid crystallised from dilute acetic acid in small plates melting at 175-176° and was identified as 7 : 8-dihydroxy-4-methyl-3-allyl-coumarin by mixed melting point with the authentic specimen prepared by the method of Naik, Desai and Desai (*loc cit.*).

5 : 7-*dihydroxy*-4-methyl-3-*β-chloropropyl-coumarin,* was prepared from phloroglucinol (1·6 g.) and the easter (2 g.), and crystallised from alcohol in needles m.p. 198-199° (decomp).

(Found Cl, 12·3 ; $C_{13}H_{13}O_4$ Cl, H_2O requires Cl, 12·4 per cent.). The coumarin dissolved with a yellow colour in alcoholic sodium ethoxide, and after warming for two hours gave 5 : 7-dihydroxy-4-

methyl-3-allylcoumarin, identified by comparison with an authentic specimen.

4 :*7-dimethyl-5-hydroxy-3-β-chloropropyl coumarin*, was obtained from orcinol and crystallised from methyl alcohol in needles m.p. 206°. (Found Cl, 12·9 : $C_{14}H_{15}O_3$ Cl requires Cl, 13·3 per cent.). It dissolved in alkali with a non-fluorescent yellow solution.

3-β-chloropropyl-4-methyl-5 : 6-α-naphtho 1 : 2-pyrone, prepared from α-naphthol, crystallised from ethyl alcohol in needles m.p. 128°. (Found Cl. 12·5 : $C_{17}H_{15}O_2$ Cl requires Cl, 12·4 per cent.) Treatment with alcoholic sodium ethoxide converted it into 3-allyl-4-methyl-5 : 6-α-naphtho-1 : 2 pyrone. Naik, Desai and Desai (*loc. Cit*).

Coumarins from ethyl-cyclohexanone-2-carboxylate. The ester was prepared from cyclohexanone by the method of Kötz[6] and boiled at 126-129°/50 mm.

7-hydroxy-cyclohexeno-(1′ : 2′ : 4 : 3)-coumarin. The mixture of cyclohexanone-2-carboxylate (2 g.), resorcinol (1·5 g.) and phosphorus oxychloride (3cc.) was slightly warmed up on the water-bath and the vigorous reaction that ensued was controlled by cooling. The deep-orange, viscous mass was stirred up with water, and the solid was crystallised from dilute ethyl alcohol when needles m.p. 203-204° were obtained. The product was identical in m.p. and mixed m.p. with the specimen prepared by Dieckmann's method (*loc. cit.*) using concentrated sulphuric acid.

7-hydroxy-X : 6 : 8-triacetoxymercuri-cyclohexeno-(1′ : 2′ : 4: 3) *coumarin.* A solution of the above coumarin (1 g.) in 5% caustic soda solution (8·0 cc.) and neutralised with 5% acetic acid (3 cc.) was gradually added to a solution of mercuric acetate (5 g.) in water (125 cc.). The cream-coloured precipitate was filtered off, redissolved in dilute alkali, filtered and acidified with acetic acid. The precipitate was filtered off on the Buchner, washed with water, and extracted several times with alcohol to remove the traces of the original coumarin, and was found to have no melting point. (Found : Hg, 60·3 ; $C_{19}H_{18}O_9Hg_3$ requires Hg, 60·6 per cent.).

5 :*7-dihydroxy-cyclohexeno-*(1′ : 2′ : 4 : 3)*-coumarin*, was similarly prepared from phloroglucinol, and crystallised from dilute alcohol in prismatic needles melting at 258° (previous sintering). The sample dried at 120° was analysed. (Found C, 67·0 ; H, 5·2 ; $C_{13}H_{12}O_4$ requires C, 67·2 ; H, 5·2 per cent). It was readily soluble in dilute alkali with a yellow, non-fluorescent solution.

Its 6 : 8 : X : *triacetoxymercuri* derivative, obtained by the above method was a grey, amorphous powder, soluble in dilute alkali, and did not melt. (Found Hg, 58·6 ; $C_{19}H_{18}O_{10}$ Hg_3H_2O requires Hg, 58·6 per cent.).

5-*hydroxy-7-methyl-cyclohexeno*-(1′ : 2′ : 4 : 3)-*coumarin*, prepared from orcinol, crystallised from alcohol in prismatic needles m.p. 242-243°. (Found C, 72·8 ; H, 6·3 ; $C_{14}H_4O_3$ requires C, 73·0 ; H, 6·1 per cent.). It was soluble in dilute alkali giving a non-fluorescent yellow solution. Mercuration gave 6 : 8 : X : *triacetoxymercuri*-derivative, which was soluble in dilute alkali and was an infusible, grey-powder. (Found Hg, 59·5 ; $C_{20}H_{20}O_9$ Hg_3 requires Hg, 59·8 per cent.).

6-*ethyl-7-hydroxy-cyclohexeno*-(1′: 2′:4 : 3)-*coumarin*, was readily obtained in a good yield from 4-ethylresorcinol, and crystallised from alcohol in prismatic needles m.p. 218°. (Found C, 73·6 ; H, 6·5 : $C_{15}H_{16}O_3$ requires C, 73·8 ; H, 6·6 per cent.). It dissolved in dilute alkali with a weak, blue fluorescence.

Our thanks are due to Dr. R. F. Hunter for his kind interest in this work.

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SYNTHESIS IN THE CHAULMOOGRIC ACID SERIES :—PART I. A NEW SYNTHESIS OF DIHYDROHYDNOCARPIC ACID

By

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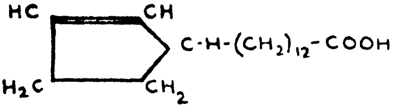
It is well-known that chaulmoogric acid (I) and its lower homologue hydnocarpic acid, (II) obtained from chaulmoogra oil, are used extensively in the form of ethyl esters or sodium salts, as the only remedy against one of the mightiest human scourge, viz., leprosy. Ever since the exact constitution of these substances was determined by Power and Barrowcliff (*J. C. S.*, 1907, 557 ; also cf. Shriner and Adams, *J.A.C.S.*, 1925, 47,2727, Perkins, *J.A.C.S.*,1926, 48. 1714), attempts were made to synthesise these important substances by the American school led by Adams and his collaborators, and scientists of Philippine leprosy research association. A considerable impetus to research in this field was given by the discovery of the relation between the physiological activity and chemical constitution. The chaulmoogric acid and the hydnocarpic acid both contain a cyclopentene ring in which the double bond is situated in the $\beta\gamma$ position with respect to the fatty acid side chain. It was found that though the presence of a double bond is not absolutely essential for possessing the physiological activity, yet the double bond, particularly in the $\beta\gamma$ position—considerably enhances the physiological activity of the molecule. (Hiers and Adams, *J. A. C. S.*, 1926, *48*, 1089, also cf. Schöbl, *Philippine J. Sci.*, 1924, *25*, 23 and 135.) Moreover hydnocarpic acid is found to be more efficacious than its higher homologue chaulmoogric acid. Adams and Sacks (*J. A. C. S.*, 1926, *48*, 2396) started from chaulmoogric acid and prepared compounds similar to chaulmoogric acid with the side chain containing upto fifteen carbon atoms, and have shown that increase in the length of the side chain led to a decrease in the physiological activity.

Chaulmoogric acid has been synthesised by Perkins and Cruz. (*J. A. C. S.*, 1927, *49*, 1070) and dihydrohydnocarpic acid has been obtained by reduction of hydnocarpic acid and also by synthesis (Adams and Noller, *J. A. C. S.*, 1926, *48*, 1074). It is the object of the present series to synthesise hydnocarpic acid and its lower homologues, and also their dihydro derivatives, to see whether the expected increase in the physiological activity due to shortening of the side chain is brought about.

The synthesis of dihydro-hydnocarpic acid by Adams and Noller (*loc. cit.*) is far too involved and lengthy, and the method of Perkins and Cruz (*loc. cit.*) cannot be applied to the synthesis of hydnocarpic acid due to the unavailability of the required ω-substituted cyano-acid-chloride. The method given below is simple and capable of giving hydnocarpic acid and dihydro-hydnocarpic acid and their lower homologues. It may also be noted that it dispenses with cyclopentenyl chloride—the starting material in Perkins and Cruzs method —a substance which is difficult to obtain and handle.

Ethyl cyclopentanone 2-carboxylate (III) was converted into its sodio derivative by treatment with powdered sodium in benzene. This on treatment with ethyl ω-bromo undecylate under all conditions gave only 5·10 per cent of the condensation product (IV). The yield of (IV) could, however, be raised to 75% if the potassio derivative of (III) is used. (IV) on boiling with concentrated hydrochloric acid was simultaneously hydrolysed and decarboxylated and gave ω-2-keto cyclopentyl undecylic acid (V). This on Clemmensen's reduction gave dihydro hydnocarpic acid (VI). The synthesis of hydnocarpic acid from (IV) by reduction, dehydration and hydrolysis is in progress.



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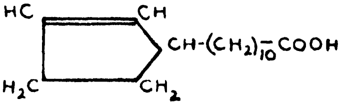

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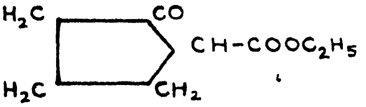

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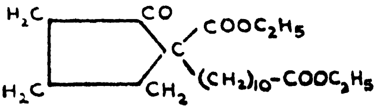

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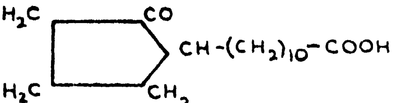

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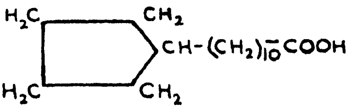

VI

EXPERIMENTAL

Ethyl cyclopentanone carboxylate was prepared according to the method of Linstead and Meade. (*J. C. S.*, 1934, 940.)

ω-bromo undecylic acid was prepared from undecylinic acid by following the method of Perkins and Cruz, (*J. A. C. S.*, 1927, *49*, 1070) using petroleum ether alone as the solvent.

Ethyl-bromo-undecylate was prepared by treating the bromo acid (93 grms.), absolute alcohol (400 grms.) and conc. H_2SO_4 (20 grms.) and refluxing the mixture on the water bath for eight hours; half the alcohol was removed, water was added and then extracted with ether. The ether extract was washed with a dilute solution of sodium carbonate, ether removed, and the residue distilled under reduced pressure.—Yield 90 per cent. B.P. 182°/12 mm. Nordlinger (B 1890. 2357), gives the b.p. as 171-172/10 mm.

Condensation of ω-bromo undecylate with ethyl cyclopentanone carboxylate :—

Potassium (5 2 grms.) was finely pulverised in toluene (60 c.c.) and poured into benzene (200 c.c.) contained in a pear shaped stout jena flask fitted with a reflux condenser carrying a $CaCl_2$ tube. Ethyl cyclopentanone 2-carboxylate (21 grms.) was gradually added when the reaction started immediately and an amount of heat was evolved with separation of the potassium salt. To complete the reaction it was heated on water bath for half an hour. Ethyl ω-bromo undecylate (39.5 grms.) was then added, and the mixture was heated for an hour and a half; about half the K-salt had reacted and no further reaction took place on heating for a longer time. The flask was, therefore, sealed and heated by immersing in a boiling water bath for six hours. A clear dark red, slightly alkaline reaction mixture was thus obtained; water was then added and the milky layer of water was removed. The benzene layer was acidified, washed with water, then Na_2CO_3 solution and finally with water; it was dried over $CaCl_2$ and benzene and toluene removed—as far as possible—on oil bath at 145°. The yield of the crude product (IV) was 50 grms.; it could not be distilled even under reduced pressure, but it did not contain any bromine.

ω-2-keto cyclopentyl undecylic acid :—

The crude diester (IV) was hydrolysed and decarboxylated by boiling with conc. HCl for 12 hours. The mineral acid was removed, the liquid was washed with water and taken with ether. The ether solution was extracted with a dilute solution of Na_2CO_3, the alkaline solution was acidified, extracted with ether, washed, dried and ether removed. The yield of (V) amounted to 22 grms.; the unhydrolysed original ester, recovered from the ether layer, was 12 grms. which on further hydrolysis gave a further yield of 6 grms. of (V)—thus making the total yield ± 28 grms (75 per cent. of the bromo-ester used.) The acid (V) was distilled under reduced pressure and came over at 230-270°/9 mm. It was refractionated, and the fraction boiling between 240-260°/9 mm. was collected.

(Found C = 71·12, H = 10·23 per cent., equi. wt. = 268·5, $C_{16}H_{28}O_3$ requires C =71·64, H =10·44 per cent., equi. wt. =268).

It gave a ***semicarbazone*** on treatment with semicarbazide acetate—m.p. 162-163° (sintering at 160°).

(Found N = 12·51 per cent. $C_{17}H_{31}O_3N_3$ requires N = 12·92 per cent.).

Reduction of the above acid (V) :—

The acid (V : 19 grms.) conc. HCl—sp. gr. 1·19—(200 grms.) and Zinc amalgam—(prepared by the modified method of Robinson and Shah, *J. C. S.*, 1934 1497 :—70 grms.) were refluxed on a sand bath for 12 hours. The solid that separated on cooling was filtered, washed, dried and crystallised from 70 per cent. alcohol. The substance melted at 50°. This was converted into its methyl ester and the liquid distilled under reduced pressure. It had b.p. 180-190°/8-9 mm. Shriner and Adams (*J. A. C. S.*, 1925, *47*, 2736-2737) give 187-188°/10 mm. as the b.p. of methyl dihydrohydnocarpate. The ester was then hydrolysed by methyl alcoholic solution of KOH ; the acid obtained on acidification was crystallised several times from 70% alcohol to a constant melting point and then again from light petroleum (40-50°), m.p. 62·5-63°. Noller and Adam (*loc. cit.*). give m.p. 63-63·5° for dihydro-hydnocarpic acid (VI).

(Found C = 75·27, per cent. H = 11·59 per cent. Equi. wt. = 254·9 ; calc for $S_{16}H_{30}O_2$, C = 75·59, H =11·81 per cent Equi. wt. =254).

Its amide—m.p. 114°—was prepared according to the method of Noller and Adams (*loc. cit.*) who give the m.p. 114·5-115·5°.

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CONSTITUTION AND DERIVATIVES OF α-PHENYL GLUTACONIC ACID

By

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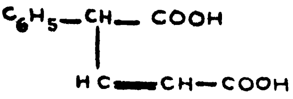
The preparation of α-phenyl glutaconic acid has been already described. [*Jour. Bom. Univ.*, 1935, part II, 106.] The structure of α-phenyl glutaconic acid, as expected from its method of synthesis, should be [I.] That it has, however, not this structure but a trans $\alpha\beta$ structure [II,] is proved by the following experimental results. (i) Oxidation of α-phenyl glutaconic acid by potassium permanganate gave benzoic acid. The production of benzoic acid is no doubt due to the further oxidation of benzoyl formic acid which must have been initially formed. (ii) α-Phenyl glutaconic acid when heated with water in a sealed tube at 100°C gave styryl acetic acid. (iii) α-phenyl-glutaconic acid is recovered unchanged by treatment with 25 per cent. potassium hydroxide solution at 100°C. If it had the structure [I] it would be expected that treatment with potassium hydroxide would shift the double bond and give an acid of structure [II] due to the conjugative effect of the phenyl group. [Cf. Linstead and Williams, *J. C. S.* 1926, 2565.] (iv) The difficulty of the formation of an anhydride of α-phenyl-glutaconic acid and the stability of the acid to boiling concentrated hydrochloride acid, may be advanced in support of trans structure. It must be admitted that all attempts to obtain cis acid from the hydroxy anhydride either by the method of Thole and Thorpe [*J. C. S.*, 1911, 2191.] or Feist [*Ann*, 1909, *370*, 41.] have been unsuccessful.

α-Phenyl glutaconic acid is unaffected by acetyl chloride at 60°C, but when heated with excess of acetyl chloride in a sealed tube at 100°C gave a mixture of hydroxy anhydride [III] and chloroanhydride [IV]. The hydroxy anhydride is fairly stable to water and can be crystallised unchanged from hot water. It does not titrate as a monobasic acid. [Contrast Thole and Thorpe [*loc. cit.*]. That it has the structure [III] is inferred from the fact that it gives a blue colouration with alcoholic ferric chloride solution, and that it dissolves unchanged in a dilute solution of sodium-bi-carbonate with deep magenta colour. [III] dissolves readily in an alkali. Acidification of its solution in alkali gives the original glutaconic acid. [III] on treatment with aniline furnishes a cis semianilide of α-phenyl glutaconic acid. The chloroanhyride [IV] is insoluble in a dilute solution of sodium carbonate but dissolves when warmed with the formation of the hydroxy anhydride.

α-Phenyl glutaconic acid when heated with aniline gave a mixture of trans semianilide and a dianilide.



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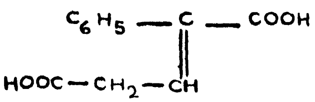

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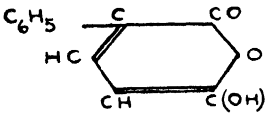

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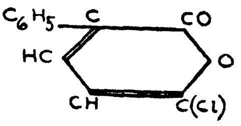

IV

EXPERIMENTAL

Salts of α-phenyl glutaconic acid :

Barium and calcium salts are soluble in water. Copper and silver salts are insoluble. The silver salt is somewhat soluble in hot water but cannot be crystallised. The *silver salt* and *copper salt* prepared from neutral ammonium salt by double decomposition and dried at 100°C were analysed.

0·1078 grams of the silver salt gave 0·0558 grams of silver on ignition.

[Found Ag = 51·11 per cent. $C_{11}H_8O_4Ag_2$ requires Ag =51·7%.] 0·1480 grams of the copper salt gave 0·0447 grams of CuO.

[Found Cu = 23·6 per cent. $C_{11}H_8O_4Cu$ requires Cu = 24·10 per cent.]

Oxidation of α-phenyl glutaconic acid :—

5 grams of the acid were just dissolved in a dilute solution of potassium carbonate and cooled. A solution of $KMnO_4$—(7·7 grams in 300 c.c. of water)— was slowly added with constant shaking. The oxidation was quick and complete in fifteen minutes. The precipitate of MnO_2 was filtered off and washed with a little distilled water. The filterate was concentrated and acidified in cold with dilute sulphuric acid, and the precipitated acid was filtered off, washed and crystallised from boiling water. It had m.p. 121°C and equivalent weight = 120·0, and was identified as benzoic acid [Mixed m.p.].

Heating α-phenyl glutaconic acid with water under pressure :—

α-Phenyl glutaconic acid [5 grams] was heated with water [30 c.c.] in a sealed tube at 160°C for six hours. On cooling the contents of the tube were extracted with ether. The ether layer was extracted with Sodium-bi-carbonate solution. The sodium-bi-carbonate extract was acidified and the precipitated acid was filtered, washed and then crystallised from hot water. It crystallised in long needles and melted at 87-88°C. Mixed m.p. with an authentic specimen of styrylacetic acid prepared according to the method of Linstead and Williams [*J. C. S.*, 1926, 2564.] was 87°C.

[Equivalent wt. found = 160·0 $C_{10}H_{10}O_4$ requires Equivalent Wt. 162·0]

Behaviour with Con. HCl :—

α-Phenyl glutaconic acid is stable to Con. HCl at 100°C. When the acid is boiled on a sand bath with Con. HCl, it is partially decarboxylated and a neutral product was obtained in small quantity. This product had b.p. 300-310°C at ordinary pressure.

[Found C = 91·80 per cent. and H = 8·48 per cent. C_9H_{10} requires C = 91·52 per cent and H = 8·48 per cent.]. It appears to be, therefore, a polymere of C_6H_5–CH = CH–CH_3.

Treatment with KOH :—

Boiling α-phenyl glutaconic acid with 10 equivalents of 25 per cent. KOH in a copper vessel brings about the complete decomposition of the acid, for on recovering the product from such a reaction a gum was obtained which could not be crystallised. But when the acid is heated in a sealed tube with 10 equivalents of 25 per cent. KOH in a boiling water bath for six hours the original acid was recovered unchanged.

Hydroxy anhydride and *chloroanhydride of α-phenyl glutaconic acid* :—

5 grams of the acid and 20 grams of acetyl chloride were heated in a sealed tube on a water bath for four hours. The contents of the tube were then transferred to an evaporating dish and the excess of acetyl chloride was removed on a water bath. To remove the last trace of acetyl chloride, it was left in a vacuum desiccator over solid potash. The product thus obtained was a mixture of chloroanhydride and hydroxyanhydride. The following procedure was adopted for their separation :— The mixture was dissolved in ether and the ether solution was repeatedly extracted with a dilute solution of sodium bi-carbonate. The bi-carbonate extract, which had a deep magenta colour, was acidified in cold with dilute

sulphuric acid. The precipitate of hydroxy-anhydride thus obtained was further purified by recrystallisation from benzene and petroleum ether. The ether layer of the above experiment on removal of ether furnished the crude chloroanhydride.

Hydroxy anhydride of α-phenyl glutaconic acid crystallises in shining needles from benzene and petrol. It is soluble in alcohol, ether and in hot water. Its aqueous solution gives a bluish violet solution with ferric chloride. It is stable to warm water and can be crystallised from hot water unchanged. It had m.p. 174-175°C. As opposed to the usual characteristic of the hydroxy anhydrides of many glutaconic acids described by Thorpe and his collaborators, it does not titrate as a monobasic acid.

[Found C = 69·5 per cent. and H = 4·00 per cent. $C_{11}H_8O_3$ requires C = 70·2 per cent and H = 4·25 per cent.]

Chloroanhydride of α-phenyl glutaconic acid was repeatedly crystallised from chloroform. It had m.p. 110-111°C. It is soluble in benzene, ether and hot chloroform. It is insoluble in sodium bicarbonate solution, and in hot water. When it is dissolved in hot sodium carbonate solution, in which it dissolves rather slowly, and then acidified, the precipitated substance was found to be the hydroxy anhydride.

[Found Cl = 16·65 per cent. $C_{11}H_7O_2Cl$ requires Cl = 16·98%.]

Cis Semianilide :—

0·8 grams of the hydroxy anhydride was treated with 0·39 grams of aniline in 10 c.c. of benzene and heated on a water bath for half an hour. It was then cooled and the benzene solution was extracted with a dilute solution of sodium bi-carbonate. On acidifying the alkaline extract a white crystalline solid separated. It was collected and purified by recrystallisation from hot water when the cis semianilide is obtained in silky needles. M. P. 156°C. It is soluble in alcohol, benzene and ether.

[Found N = 4·9 per cent. $C_{17}H_{15}O_3N$ requires N = 4·98 per cent.]

Trans semianilide and the dianilide of α-phenyl glutaconic acid :—

1 gram of the acid was heated with 0·45 grams of aniline at 150° for ten minutes. The product on cooling was taken up in ether and extracted with a dilute solution of sodium bi-carbonate and the extract was acidified when a solid separated. It was purified by recrystallisation from hot water. *Trans semianilide* is soluble in ether, benzene and alcohol. It was obtained from hot water in long needles. M.P. 96°C.

[Found N = 4·92 per cent. $C_{17}H_{15}O_3N$ requires N = 4·98 per cent.]

Dianilide of α-phenyl glutaconic acid was obtained from the ether layer in the above experiment. The ether layer was washed with water and ether removed. The residue was crystallised from dilute alcohol. It had m.p. 90°C.

[Found N = 7·8 per cent. $C_{23}H_{20}O_2\,N_2$ requires N = 7·86 %.]

We thank Mr.K.V.Bokil and Dr.M.S.Shah for their interest in this work and the University of Bombay for a research grant to one of us (K.S.N.).

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PHENYLGLUTARIC ACIDS. PART II. β-PHENYL-β-METHYLGLUTARIC ACID

By

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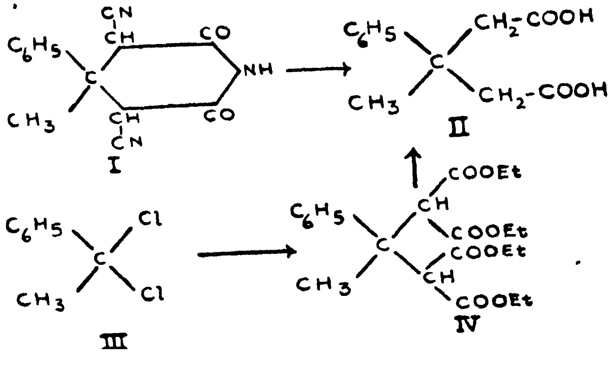
The object of synthesising these acids is indicated in part I (*Jour. Bom. Univ.*, 1936, part II, p. 105). The synthesis of β-phenyl β-methyl glutaric acid has been an unusually difficult task, and as yet no satisfactory method has been found to prepare it in quantity. The Michael addition of ethyl malonate to ethyl β-methyl cinnamate was unsuccessful. The condensation of acetophenone with cyanacetamide under the conditions of Thorpe (*J.C.S.*, 1919, 686.) could not be accomplished. The condensation of acetophenone with ethyl cyanoacetate under the conditions of Guareschi (Atti. R. *Acad. Sci.* Torino, 1900-1901, *36*, 443.) proceeded but the yield of imide (I) was very low. The imide on hydrolysis gave β-phenyl β-methylglutaric acid Attempts were made to prepare the same acid by the method developed in part I. (*loc. cit.*) Acetophenone chloride (III) was condensed with sodio derivative of ethyl malonate and worked up in the usual way. The condensation product (IV) without further purification was hydrolysed by boiling hydrochloric acid when β-phenyl β-methylglutaric acid (II) was obtained again in very small yield. The low yield in this case is no doubt due to the small amount of acetophenone chloride present in the mixture obtained by treating acetophenone with phosphorus pentachloride. (Cf. Tayler *J. C. S.* 1937, 304). Due to scarcity of material it was not possible to prepare the usual derivatives of β-phenyl β-methylglutaric acid.



EXPERIMENTAL

Preparation of *cyano-imide* (I) :—To a mixture of acetophenone (40 gm) and ethyl cyanoacetate (56·5 gms.), was added a saturated solution of dry ammonia in absolute alcohol (50 c.c.). It was left in cold for 48 hours. The solid that had separated was filtered and washed with ether. It was then dissolved in water and acidified when the imide (I) separated which was filtered and dried. Yield 2·0 gms. Nothing could be obtained from the mother liquor left after separating the solid. The imide had m.p. 270°C. (Found N = 16·10, $C_{14}H_{11}O_2N_3$ requires N = 16·60 per cent.)

β-Phenyl β-methylglutaric acid :— The imide (1·5 gms.) was dissolved in concentrated H_2SO_4 (2 c.c.), water (1.5 c.c.) was then added and boiled for half an hour. It was cooled and extracted with ether, dried and ether removed. The residue (0·4 gms.) was crystallised from hot water in fine needles. It was soluble in hot water, alcohol, benzene and insoluble in petrol and had m.p. 132-133°C. (Found :— C = 64·69 and H = 6·42 per cent. Equivalent wt. =112·0. $C_{12}H_{14}O_4$ requires C = 64·86 and H = 6·30 per cent. and Equi. wt. = 111).

Ba and Ca salts of β-phenyl β-methylglutaric acid are soluble in water. The *silver* salt is insoluble in water. The silver salt was analysed. (Found Ag = 49·23 per cent. $C_{12}H_{12}O_4Ag_2$ requires Ag =49·54 per cent.)

Acetophenone chloride :—A mixture of acetophenone (10 gms.) and PCl_5 (19 gms.) was kept at 40° for one hour. It was then poured in ice water and left till practically the whole of $POCl_3$ had decomposed. The oil that had separated was dried over $CaCl_2$ and used without distillation as it was found that this crude substance gave better yields.

Condensation of acetophenone chloride with ethyl sodio-malonate :— Acetophenone chloride (18 gms.) was added to ethyl sodio malonate prepared from sodium (4·6 gms.) ethyl malonate (32 gms.) in benzene (100 c.c.) It was then sealed and heated in a water bath at 100°C for six hours. Water was then added, benzene layer separated, washed with a dilute solution of sodium carbonate, dried and benzene removed. The residue could not be distilled without decomposition under reduced pressure. It was, therefore, hydrolysed by boiling with five times its quantity of concentrated hydrochloric acid. The cooled product was taken up in ether washed with water and extracted with sodium carbonate solution. The extract on acidifying gave a semisolid mass (0·5 gms.) which on recrystallisation from hot water was obtained in needles and had m.p. 132°C and did not depress the m.p. of the acid obtained from imide (I).

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A NOTE OF CRITICISM ON THE SYNTHESIS BY DIXIT OF βP-HYDROXY (OR P-METHOXY)—PHENYL-GLUTACONIC ACID FROM THE CORRESPONDING GLUTARIC ACID

By

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In connection with our work on α-phenylglutaconic acid we were interested to know whether the same could be prepared by brominating α-phenylglutaric acid and then eliminating a molecule of hydrobromic acid from the bromo acid or its ethyl ester. That such a method is available for the preparation of β-alkylated glutaconic acids was shown by Derbyshire and Thorpe. (*J. C. S.* 1905, 1714.) The method, however, is not available for the preparation of β-phenyl glutaconic acid. Haerdi and Thorpe (*J.C.S.* 1925, 1237.) have shown that α-bromo β-phenyl glutaric acid, obtained by brominating β-phenyl glutaric acid, contained an active bromine atom, and in consequence no trace of β-phenyl glutaconic acid was obtained in all attempts to eliminate hydrobromic acid from the bromo acid or its methyl ester. Dixit, (*Jour.Ind.Chem.Soc.*1931, 787.) however, claims to have synthesised β4-hydroxy—(or 4-methoxy)—phenyl-glutaconic acid by brominating the esters of the corresponding glutaric acids and then eliminating hydrobromic acid from the ethyl esters of the bromo-acids. This seemed to us unlikely as the compounds handled by Dixit differed from that of Haerdi and Thrope in having a p-hydroxyl (or p-methoxyl) group only. Hence we wanted to know the details of the experimental procedure followed by Dixit. The publication (Dixit *loc. cit.*) gives no details, the only sentence referring to it being that Derbyshire and Thorpe's method was followed. The following details are found in the thesis which Dixit submitted to the University of Bombay. (Bombay University Thesis for M.Sc.No 111. p. 66.) " 7 gms. of β4-hydroxy-phenyl-glutaric ester were mixed with 5·5 gms of phosphorus pentabromide. The mixture was heated under a protected reflux condenser for six hours. The liquid contents were cooled and poured into excess of petroleum ether and kept overnight. The oil which separated was extracted on next day by ether and the ethereal solution was washed out by concentrated sodium hydroxide and the washing were acidified. The oil which separated was again extracted. It was then distilled under reduced pressure. Yield 3·2 gms. Thick brown liquid with pungent smell b. p. 230°C at 21 mm. This was the monobromo ester." The method described in case of p-methoxy compound is slightly different. "The reaction product obtained from 10 gms. of ethyl 4-methoxy-phenyl-glutarate and phosphorus pentabromide (7 gms.) was poured in petroleum ether and kept overnight. It was then extracted with ordinary ether. The etheral solution was dried and ether removed and the residue distilled under reduced pressure. Yield 10·5 gms. b. p. 246°C at 21 mm. Thick brown oil of disagreeable odour." (Dixit's thesis *loc. cit.* p. 69.)

The anomaly in the above experiments appears to be how phosphorus pentabromide used in less than molecular proportion could effect the bromination of the methylene group without affecting the ester groups or the hydroxyl group or brominating the phenyl nucleus.

Dixit claims to have followed the method of Derbyshire and Thorpe, but it appears that he did not go through the details of procedure as laid down by the above authors. Derbyshire and Thorpe treated the anhydride of the glutaric acid with phosphorus pentabromide in order to convert the anhydride into acid bromide. (The ester could also be used provided two molecular proportions of phosphorus pentabromide are taken.). They then treated it with bromine to brominate the methylene group. The reaction mixture was poured in absolute alcohol to convert the acid bromide groups into ester groups. It was then worked up in the usual way.

It is obvious that Dixit could not have obtained the ethyl ester of the bromo acid by the procedure he followed. This has now been experimentally verified. The work on βp-hydroxy-phenyl-glutaric acid was not repeated in order to avoid the complication due to the free hydroxyl group. Ethyl βp-methoxy-phenyl glutarate when treated according to the method of Dixit gave unchanged ester, p-methoxyl-phenyl glutaric acid and ethyl 3 bromo-4-methoxy-phenyl glutarate.

EXPERIMENTAL

Ethyl β4-methoxy-phenyl glutarate was prepared by esterifying the corresponding acid by Fischer Speier method and had b.p. 325-330°C at ordinary pressure and 210°C at 10 mm. (Compare Jackson and Kenner *J. C. S.* 1926, 1660.)

Ethyl β4-methoxy-phenyl glutarate (10 gms.) was mixed with phosphorus pentabromide (7 gms.) and the mixture heated on a water bath for six hours with a protected reflux condenser. The cooled product was poured in petroleum ether and left overnight. The small amount of oil that had separated was taken up in ether, washed by a dilute solution of sodium carbonate, dried over calcium chloride and ether removed and the residue distilled under reduced pressure. Yield 3·8 gms. b. p. 246°C at 21 mm. It was a colourless liquid of agreeable odour and contained bromine. (Found Br = 9·16 per cent. while $C_{16}H_{21}O_5$ Br requires Br = 21·5 per cent.) On hydrolysis by alkali in cold it gave a mixture of acids, from which β4-methoxy-phenyl-glutaric acid m. p. 163°C and β3-bromo-4-methoxy-phenyl-glutaric acid m. p. 147°C (Limaye and Chitre *Jour. Bom. Univ.* 1935, part II, Vol. IV p. 97.) were isolated by fractional crystallisation and identified.

The sodium carbonate extract in the above experiment on acidifying gave a small amount of β4-methoxy-phenyl-glutaric acid.

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FLAVONE DERIVATIVES FROM GLYCEROL ETHERS OF RESACETOPHENONE

By

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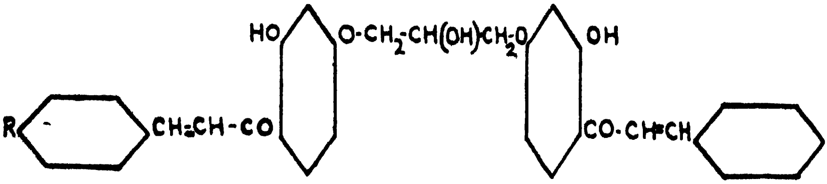
Motwani and Wheeler (*J. C. S.*, 1935, 1098) studied the preparation of β-hydroxyethyl ethers of resacetophenone with a view to synthesising substances containing coumaran and γ-pyrone nuclei. The present authors (*J. C. S.*, 1936, 589). synthesised a number of glycerol ethers of resacetophenone, and these have now been employed in the synthesis of flavone derivatives of the type prepared by Motwani and Wheeler (*loc. cit.*).

2-Hydroxy-4-(βγ-dihydroxypropoxy)acetophenone (Nadkarni and Wheeler, *loc. cit.*) has been condensed with benzaldehyde, *p*-anisaldehyde and salicylaldehyde to give the corresponding *chalkones*, respectively, 2-*hydroxy*-4-(*βγ-dihydroxypropoxy*)*phenyl styryl ketone*, (I), 2-*hydroxy*-4-(*βγ-dihydroxypropoxy*) *phenyl* 4-*methoxystyryl ketone*, (II), and 2-*hydroxy*-4-(*βγ-dihydroxypropoxy*) *phenyl* 2-*hydroxystyryl ketone* (III).

(I) and (II) on treatment with selenium dioxide gave the corresponding *flavones* (Mahal, Rai and Venkataraman, *J. C. S.*, 1935, 866) ; the constitution of the flavone from (I) was confirmed by its depropylation with hydrogen iodide to 7-hydroxyflavone. These two chalkones with alkaline hydrogen peroxide yielded the corresponding *flavonols* (cf. Algar and Flynn, *Proc. Roy Irish Acad.*, 1934, 42*B*, (1) ; Oyamada, *J. Chem. Soc. Japan*, 1934, *55*, 1256 ; Murakami and Irie, *Proc. Imp. Acad.* (Tokyo), 1935, *11*, 229 ; the hydroxylated side chain was not attacked.

(I) and (II) with bromine gave *bromochalkone dibromides* which were hydrolysed by Kostanecki's method to the corresponding *bromo-flavones*. The position of the nuclear bromine atom is established by studying the products of hydrolysis, obtained by heating the bromo-flavone with sodium ethoxide in alcoholic solution. (Cf. Kostanecki and Ludwig, *Ber.*, 1898, *31*, 2951). The absence of benzylidenecoumaranones in the products was confirmed by the colour reactions with sulphuric acid. (See Kostanecki, *Bull. Soc. chim.*, 1903, (iii) *29*, *Supp.*)

Glyceryl αγ-bis- (3-hydroxy-4-acetylphenyl) ether, (Nadkarni and Wheeler, *loc. cit.*) gave with benzaldehyde the *dichalkone* (IV; R = H) and with anisaldehyde (IV R = OMe). It was not found possible to convert these dichalkones to flavone derivatives.



IV

EXPERIMENTAL

2-Hydroxy-4-(βγ-dihydroxypropoxy) phenyl-styryl ketone. (I)

A mixture of 2-hydroxy-4-(βγ-dihydroxypropoxy) acetophenone (25 g.) (*J. C. S.* 1936 590) and benzaldehyde (11·7 g.) in alcohol (200 ccs.) was treated with aqueous potassium hydroxide (40%; 60 ccs.) and after twenty-four hours, the whole was diluted and acidified with acetic acid. The precipitated *chalkone* (28 g.) crystallised from a mixture of chloroform and light petroleum in yellow needles, m.p. 120°. (Found : C, 68-6; H, 5·7. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%).

2-Hydroxy-4-(βγ-dihydroxypropoxy)phenyl 4-methoxy-styryl ketone. (II):

A mixture of 2-hydroxy-4-(βγ-dihydroxypropoxy) acetophenone (11·3 g.), *p-anisaldehyde* (6·8 g.) in *alcohol* (125 ccs.) and aqueous potassium hydroxide (40%, 35 ccs.) was kept for 30 hours. The *chalkone* (12·5 g.) obtained on acidification with acetic acid crystallised from alcohol in yellow needles, m.p. 153°. (Found: C, 65·8; H, 5·8; $C_{19}H_{20}O_6$ requires C, 66·3, H, 5·8%).

2-Hydroxy-4-(βγ-dihydroxypropoxy)phenyl 2-hydroxy-styryl ketone. (III):

A mixture of salicylaldehyde (6·1 g.), 2-hydroxy-4-(βγ-dihydroxy-propoxy)acetophenone (11·3 g.) in alcohol (100 ccs.) and aqueous potassium hydroxide (40%, 30 ccs.) was kept at 60° for 30 hours and then diluted and acidified with acetic acid. The precipitated *chalkone* crystallised from glacial acetic acid in yellow needles, m.p. 182°. (Found: C, 65·1; H, 5·5; $C_{18}H_{18}O_6$ requires C, 65·5 H, 5·5%).

7-(βγ-dihydroxypropoxy) flavone :

A mixture of (I, 2·5 g.), selenium dioxide (3 g.) and amyl alcohol (30 ccs.) was heated at 150° under reflux, for 12 hours. After removal of the selenium by filtration, the amyl alcohol was removed by distillation with steam. The pale yellow residue (1 g.) crystallised from alcohol in long shining needles, m.p. 87-88°. Its colourless solution in concentrated sulphuric acid showed blue fluorescence. The product contained two molecules of water of crystallisation. (Found : C, 62·5 ; H, 5·9 ; loss at 150°/2m.m. 10·5 ; $C_{18}H_{16}O_5$, $2H_2O$ requires C, 62·1 : H, 5·8% and loss 10·4%. After drying at 150° high vacuum, found C, 68-6 ; H, 5·3 ; $C_{18}H_{16}O_5$ requires C, 69·2 ; H, 5·1%).

De-propylation of the flavone :

A solution of the flavone (0·3 g.) in acetic anhydride (15 ccs.) was boiled with hydriodic acid (d 1·7 ; 10 ccs.) for 1½ hours. The solid which separated on pouring the mixture into a concentrated solution of potassium hydrogen sulphite was crystallised from rectified spirit ; m.p. 239-240°, not depressed when mixed with an authentic specimen of 7-hydroxyflavone.

4′-methoxy-7-(βγ-dihydroxypropoxy) flavone :

A mixture of (II, 3 g.), selenium dioxide (3·5 g.) and amyl alcohol (30 ccs.) was heated at 150° under reflux for 8 hours. After filtration amyl alcohol was evaporated in steam. The yellow ressidue (1 g.) crystallised from alcohol in pale yellow shining needles, m.p. 92-94°, giving a pale yellow solution with blue fluorescence in concentrated sulphuric acid. It contained three molecules of water of crystallisation. (Found : C, 57·7 ; H, 6·0 ; loss at 150°/2 m.m. 13·8. $C_{19}H_{18}O_6$, $3H_2O$ requires C, 57·6 ; H, 6·0 and loss 13·6%). After drying at 150° high vacuum, found : C, 66·3 ; H, 5·2 ; $C_{19}H_{18}O_6$ requires C, 66·7 ; H, 5·3%.)

7-(βγ-dihydroxypropoxy) flavonol :

A mixture of (I, 2 g.) in alcohol (20 ccs.) and N/2 alcoholic caustic potash (18 ccs.) was gradually treated with hydrogen peroxide (6%, 10 ccs.) with shaking, and ,was kept until the orange colour of the mixture had changed to pale yellow (two hours). The whole was diluted and acidified with dilute sulphuric acid. The precipitated *flavonol* (0·8 g.) crystallised from alocohol in pale yellow needles, m.p. 153-155°, giving a green fluorescence with concentrated sulphuric acid, and violet coloration with alcoholic ferric chloride. (Found : C, 65·7 ; H, 5·0 ; $C_{18}H_{16}O_6$ requires C, 65·9 ; H, 4·9%).

4′-methoxy-7-(βγ-dihydroxypropoxy)flavonol :

Hydrogen peroxide (6% ; 12 ccs.) was added gradually with shaking to a hot solution of (II, 2 g.) in alcohol (25 ccs.) and N/2 alcoholic caustic potash (22 ccs.) After three hours, when the orange colour of the solution had changed to yellow, the whole was diluted and acidified with dilute sulphuric acid. The precipitated *flavonol* (0·8 g.) crystallised from alcohol in long yellow shining needles, m.p. 195°. It gave a green fluorescence in concentrated sulphuric acid, and a violet coloration with alcoholic ferric chloride. (Found : C, 63·8 ; H, 5·1 ; $C_{19}H_{18}O_7$ requires C, 63·7 ; H, 5·0%).

5-*Bromo*-2-*hydroxy*-4-(*βγ-dihydroxypropoxy*)*phenyl αβ-dibromo-β-phenylethyl ketone* (2·9g.) separated from a solution of bromine (6 g.) and (I, 5·6 g.) in chloroform (35 ccs.). It crystallised from acetone in needles, m. p. 200° (Found Br, 43·6 ; $C_{18}H_{17}O_5Br_3$ requires Br, 43·4%).

6-*Bromo*-7-(*βγ-dihydroxyproproxy*)*flavone* (1·1 g. separated when the above dibromide (2 g.) in alcoholic suspension (30 ccs.) was shaken at room temperature with aqueous sodium hydroxide (8% ; 35 ccs.). It crystallised from alcohol in needles, m. p. 156-157°, which gave a yellow solution with concentrated sulphuric acid. (Found Br, 20·8 ; $C_{18}H_{15}O_5Br$ requires Br, 20·5%.)

6-*Bromo*-4-*methoxy*-7-(*βγ-dihydroxypropoxy*)*flavone* (0·4 g.)was formed by the hydrolysis of the pasty dibromide obtained by bromination of (II, 4 g.) in chloroform. It crystallised from alcohol in yellow needles, which gave a yellow solution with green fluorescence with concentrated sulphuric acid, m.p. 116-117° (Found Br, 19·4 ; $C_{19}H_{17}O_8Br$ requires Br, 19·0%).

This bromoflavone was hydrolysed by Kostanecki and Ludwig's method (*loc. cit.*). A mixture of the bromoflavone (0·3 g.), sodium (1 g.) and alcohol (25 ccs.) was refluxed for six hours. The whole was acidified with dilute sulphuric acid, and the solid residue which separated was extracted with sodium carbonate solution. The filtrate was acidified and extracted with ether, which gave anisic acid, m. p. 182-183°, not depressed when mixed with an authentic specimen of anisic acid. The bromine atom was therefore in the chromone ring. The position of the bromine atom is established by a consideration of the orienting influences of the other groups present in the ring. (Cf. Cullinane and Philpott, J. C. S., 1929, 1763).

Glycerol-αγ-bis-(3-*hydroxy*-4-*benzylideneacetylphenyl*) ether.

A mixture of αγ-bis-(3-hydroxy-4-acetylphenyl) ether (20 g.) in alcohol (300 ccs.), benzaldehyde (12 g.) and aqueous potassium hydroxide (40%, 60 ccs.) was kept at 60° for three hours. After thirty hours when the potassium salt had separated, the whole was diluted and acidified with acetic acid. The resulting *chalkone* (21 g.) crystallised from acetic acid, m. p. 210°. (Found C, 73·7 ; H, 5·5 ; $C_{33}H_{28}O_7$ requires C, 73·9 ; H, 5·2 %).

Glycerol-αγ-bis-(3-hydroxy-4-p-anisylideneacetylphenyl) ether :

A mixture of αγ-bis-(3-hydroxy-4-acetylphenyl) ether (12 g.) in alocohol (200 ccs.), *p*-anisyldehyde (9·2 g.) and potassium hydroxide (40%, 50 ccs.) was kept at 60° for three hours. After 40 hours when the potassium salt had separated, the whole was diluted and acidified with acetic acid. The solid *chalkone* (12 g.) crystallised from acetic acid, m. p. 200-1° (Found C, 70·1 ; H, 5·3 ; $C_{35}H_{32}O_9$ requires C. 70·5 ; H, 5·4%).

Acknowledgment is made to the Dabholkar Research Scholarship Trust for a scholarship and to the University of Bombay for a grant to one of us (D. R. N.) towards the expenses of this investigation.

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REACTIVITY OF FORMIC ACID :—A METHOD OF ESTIMATING SIDE-CHAIN HALOGEN IN AROMATIC COMPOUNDS

By

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Formic acid is well known to react with phosphorus pentachloride or thionyl chloride to give hydrogen chloride and carbon monoxide, presumably through the intermediate formation of formyl chloride. It has now been found that compounds containing less active halogen such as benzyl chloride, benzal chloride and benzotrichloride react similarly with formic acid. This reaction can be used as the basis of a convenient method for the estimation of side-chain halogen in aromatic compounds.

EXPERIMENTAL

The reaction with benzotrichloride was studied in detail. Weighed quantities of benzotrichloride (fractionated at reduced pressure) and Kahlbaum's purest anhydrous formic acid were heated at 100° under reflux until evolution of hydrogen chloride and carbon monoxide had ceased. With excess of formic acid no benzotrichloride remained and benzoic acid separated on dilution and cooling. When formic acid was not in excess, the product was treated with dilute sodium hydrogen carbonate solution, benzotrichloride was extracted with ether and benzoic acid was precipitated with hydrochloride acid. The conversion of benzotrichloride into benzoic acid with 1·5, 2, and 3 molecular proportions of formic acid was about 51%, 85%, and 95% respectively. Fractionation of the product obtained with 1 molecular proportion of formic acid gave benzoyl chloride and benzoic acid. Benzoyl chloride, and acetyl chloride, reacted readily with formic acid to give the corresponding acids, hydrogen chloride, and carbon monoxide. These results indicate that the reaction is as follows :—

$$C_6H_5CCl_3 + HCOOH \rightarrow C_6H_5COCl + 2HCl + CO$$

$$C_6H_5COCl + HCOOH \rightarrow C_6H_5COOH + HCl + CO$$

Benzal chloride when heated with formic acid gave benzaldehyde, hydrogen chloride, and carbon monoxide ; benzyl chloride also gave hydrogen chloride and carbon monoxide, but benzyl alcohol was not isolated; presumably it reacted with formic acid.

For the quantitative examination of the reaction, weighed quantities of the chlorides were heated at 100° with excess of formic acid in a current of purified nitrogen which was then led through dilute silver nitrate solution. 97% of the chlorine in benzotrichloride was recovered in 30 mins. Reaction with benzyl chloride was slower. The attempt to carry out the reaction in this way was not pursued as it was found that quantitative results were more readily obtained by using a solution of sodium formate in formic acid. The procedure eventually developed is as follows:—0·1 to 0·3 g. of the halide is heated on the water-bath with sodium formate (about 1 g.) dissolved in anhydrous formic acid (10 c.c.). After 3 hours the mixture is rapidly cooled and poured into a solution of silver nitrate (1 g.) in nitric acid (5 c.c. conc.) and water (10 c.c.). The precipitated halide is collected in a Gooch crucible, washed with water and with acetone to remove any organic matter, dried and weighed. Table I shows some results of the application of the new method.

TABLE

Substance.	Side-chain halogen	
	per cent. found.	per cent required
Benzyl chloride	27·4 ; 27·6	28·0
Benzyl bromide	46·7 ; 46·6	46·8
Benzal chloride	44·1 ; 43·9	44·1
Benzotrichloride	54·1 ; 54·2 ; 54·3.	54·5
*3-Chloro-4-methoxy-benzyl bromide	33·9	34·0
*3-Bromo-4-methoxy-benzyl chloride	15·0	15·1
*3-Bromo-4-methoxy-benzyl bromide	28·6 ; 28·7	28·6
* 6-Chloro-piperonyl chloride	17·1	17·3
*6-Chloro-3 : 4-carbonyldioxy-benzyl chloride	15·8	16·2
*6-Chloro-piperonyl bromide	31·5	32·0
*6-Bromopiperonyl bromide	27·4	27·2

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* Prepared by Mr. R. G. Naik in this laboratory in connection with another research.

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CONDENSATION OF CHLORAL WITH URETHANES: A STUDY OF THE GROUP MH. CHOH. C. CL_3

By

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Jacobson (*Ann.* 1871, 157, 246) prepared monochloral urea and dichloral urea by condensing chloral with urea. Coppin and Titherley (*J. C. S.*, 1914, 105, 32) obtained the same compounds and assigned them the following constitutions: (1) monochloral urea: $C. Cl_3$. CHOH. NH. CO. NH_2; (2) dichloral urea: $C. Cl_3$. CHOH. NH. CO. NH. CHOH. $C.Cl_3$, the latter being obtained only in the presence of hydrochloric acid. Feist (*Ber.* 1912, 45, 953) and Bischoff (*Ber.* 1874, 7, 631) condensed chloral with methyl and ethyl urethanes, respectively, using concentrated hydrochloric acid.

The present paper is a study of chloralpropyl and iso-butyl-urethanes and their various derivatives such as anhydro, acetoxy, benzoyloxy and methoxy.

EXPERIMENTAL

Chloralpropylurethane :—

Concentrated hydrochloric acid (10 cc.) was added to a mixture of chloral (45 g.) and propylurethane (30 g.) when a clear solution, from which a crystalline solid (70 g.) separated was obtained. The product crystallised from petrol ether in small needles, m. p. 75°. (Found : Cl, 42·3 ; $C_6H_{10}O_3NCl_3$ requires Cl, 42·5 per. cent.).

Chloral-iso-butylurethane was similarly prepared. It crystallised from petrol ether in plates, m. p. 116°. (Found : Cl, 40·1 ; $C_7H_{12}O_3NCl_3$ requires Cl, 40·3 per cent.).

Methyl ether of chloralpropylurethane was prepared by the method of Diels and Seib (*Ber.* 1909, 42, 4066).

Sodium methylate (0·4 g. Na. in 20 cc. methyl alcohol) was added to anhydro-chloralpropylurethane (3 g.) dissolved in methyl alcohol (20 cc.) and the mixture warmed on a water bath for half an hour at 50°. On cooling it was diluted with water, when an oil separated which slowly solidified (1·4 g.). It crystallised from petrol ether in needles, m. p. 57-8°.

(Found : Cl, 40·0 ; $C_7H_{12}O_3NCl_3$ requires Cl, 40·3 per. cent.).

Methyl ether of chloral-iso-butylurethane was prepared as above. It crystallised from methyl alcohol in shining plates, m. p. 66-7°.

(Found : Cl. 38·0 ; $C_8H_{14}O_3NCl_3$ requires Cl. 38·2 per cent.).

The anhydro derivatives (Nos. 1 & 2) of the chloralpropyl and isobutylurethanes were prepared by adding at 0°, to their solution in dil. NaOH, acetic anhydride drop by drop, till the solution became acidic and an oily product separated which soon solidified.

The acetyl derivatives (Nos. 3 to 6) of the chloralmethyl-,ethyl-, propyl-, and isobutyl-urethanes were prepared by adding a few drops of con. sulphuric acid to a mixture of the chloral urethane and acetic anhydride, keeping the mixture overnight and then diluting with water.

The benzoyl derivatives (Nos. 7 to 10) of the chloral-methyl-, ethyl-, propyl-, and isobutyl-urethanes were prepared by adding benzoyl chloride to a solution of the chloral urethane in pyridine and then refluxing the mixture on water bath for an hour and pouring it into dil. HCl.

Name.	Formula.	Crystallised from.	Appearance.	M.P.	Analysis.	
					Found	Required
(1) Anhydro-chloral propylurethane.	$C_{12}H_{18}O_5N_2Cl_6$	Methyl alcohol	Needles	94.5°	Cl,43·9	44 per cent.
(2) Anhydro-chloral iso-butyl-urethane.	$C_{14}H_{22}O_5N_2Cl_6$	Petrol ether	Clusters of needles.	106-7°	Cl,41·6	41·7 „ „
Acetyl derivatives of:—						
(3) Chloralmethylurethane.	$C_6H_8O_4NCl_3$	Methyl alcohol	„	54.5°	Cl,40·1	40·3 „ „
(4) Chloralethylurethane.	$C_7H_{10}O_4NCl_3$		Oil	B.P. 155-59°/16 mm.	Cl,38·2	38·2 ‘, „
(5) Choralpropylurethane.	$C_8H_{12}O_4NCl_3$		Oil	E.P. 150-53°/17 mm.	Cl,36·5	36·4 „ „
(6) Chloral-iso-butylurethane.	$C_9H_{14}O_4NCl_3$	Benzene	Tiny needles.	M.P. 59-61°.	Cl,34·8	34·7 „ „
Benzoyl derivatives of:-						
(7) Chloralmethylurethane.	$C_{11}H_{10}O_4NCl_3$	Methyl alcohol	Feathery needles.	178-9°	Cl,32·4	32·6 „ „
(8) Chloralethylurethane.	.$C_{12}H_{12}O_4NCl_3$	„ „	Rhombic plates.	126-27°	Cl,31,3	31·3 „ „
(9) Chloralpropylurethane.	$C_{13}H_{14}O_4NCl_3$	„ „	Tiny needles.	99-100°	Cl,29·8	30·0 „ „
(10) Chloral-iso butylurethane.	$C_{14}H_{16}O_4NCl_3$	Benzene	„	122-23°	Cl,28·8	28·9 „ „

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NUCLEAR CONDENSATION PRODUCTS OF CHLORAL WITH PHENOLS

By

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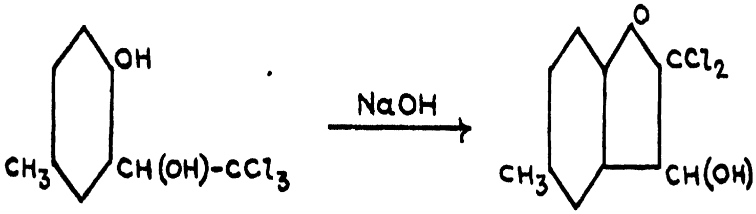
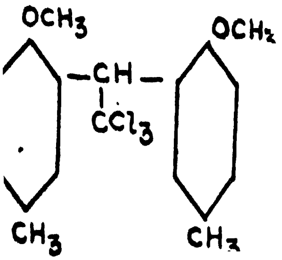
The nuclear condensation products with phenols have been prepared according to Pauly and Schanz (*Ber.* 1923, 56, 979), chloral hydrate being replaced by chloral, which accelerates the reaction.

Chloral usually condenses in para position to —OH. If this is occupied, it enters the ortho; since the *p*-cresol condensation product I yielded a coumarone derivative II on treatment with alkali.

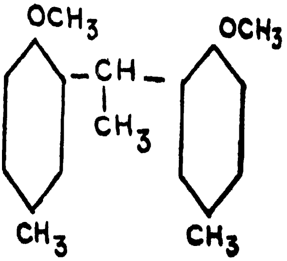


I II

Condensation was also attempted in presence of sulphuric acid, but no definite product was obtained except with *p*-cresol methyl ether, which gave compound III (cf. Baeyer, *Ber.* 1872, 5, 1098); III on reduction gave IV.



III



IV

Various other acetyl, benzoyl and methoxy derivatives of the condensation products with phenol, resorcinol, guiacol and *p*-cresol have been studied. The acetoxy R.CH(OAc) CCl_3 and the benzoyloxy R. CH(OBz)CCl_3 groups in the side chain when reduced with zinc and acetic acid give R. CH_2CHCl_2, while the methoxy R. CH (OMe) CCl_3 gives RCH(OMe)$CHCl_2$. The reduction products are isolated by pouring the reaction mixture in water.

A new condensation product of two molecules of chloral with one of resorcinol is also described.

EXPERIMENTAL

In the condensation of chloral with various phenols (Phenol, Resorcinol, Guiacol and *p*-Cresol), the various proportions used and time required are tabulated below, potassium carbonate being used as a condensing agent.

Condensations.	Phenol	Chloral	Time	Temp.	Yield.
Phenol ...	94 g.	147 g.	one month	Room temp.	60 g. Sticky solid
Resorcinol ..	80 g.	120 g.	7 days	below 5°	... mixture in benzene (200 cc.)
Resorcinol ...	110 g.	295 g	7 days	„	...
Guiacol ...	124 g.	147 g.	1½ month	Room temp.	...
p-Cresol ...	108 g.	147 g.	three weeks	„	75 g.

The simple derivatives are described in the table above.

Reaction of alkali on p-*cresol condensation product.*

1 : 1 *Dichloro-2-hydroxy-4-methyldihydro-coumarone* II.

The *p*-cresol condensation product I (20 g.) when treated with sodium hydroxide solution (200 c.c. 20%) for half an hour gave a yellow solid, which was washed with water. It recrystallised from alcohol in thin needles ; m.p. 182°. It contains a molecule of alcohol of crystallisation, which is removed on heating at 110°. (Found . C_2H_5OH, 17·9 ; Cl, 26·5 ; $C_9H_8O_2Cl_2$, C_2H_5OH requires C_2H_5OH, 17·4, Cl, 26·8 per cent.

Condensation of p-*cresyl methyl-ether with chloral in presence of sulphuric acid* :

ααα-Trichloro-ββ-di-(2-methoxy-5-tolyl)ethane III.

p-cresyl methyl ether (61 g.) and chloral (74 g.) were mixed, when heat was evolved. On cooling, sulphuric acid (200 c.c.) was added. After six hours, a crystalline solid separated. The mixture was poured over ice and the solid separated was crystallised from acetic acid : long colourless plates : m.p. 161°. Yield 60 g. (Found : Cl. 28·3, $C_{18}H_{19}O_2Cl_3$ requires Cl, 28·5 per cent).

Reduction :

αα-Di-(2-methoxy-5-tolyl) ethane IV.

The above product (30 g.) was shaken with acetic acid (200 cc.), zinc dust (15 g.) being added at intervals. On pouring this mixture over ice, an oil separated, which was extracted with ether. It distilled at 185°/10 m.m. (Found : C, 79·6 ; H, 7·9 ; $C_{18}H_{22}O_2$ requires C, 80·0 ; H, 8·1 per cent.)

Derivatives of 4-hydroxy-(β β β - trichloro- α -hydroxy)ethylbenzene.

Name.	Formula	Crystalline nature.	m. p.	Analysis	
				found	required
1. Di acetoxy	$OAc.C_6H_4.CH(OAc)CCl_3$	...	155°	Cl,32.7	Cl,32.7
2. Di benzoyloxy	$OBz.C_6H_4.CH(OBz)CCl_3$	...	132°	Cl.23.8	Cl,23.7
3. Di methoxy	$OMe.C_6H_4.CH(OMe)CCl_3$	Liquid	185°/25 m. m.	Cl,39.4	Cl,39.5
4. Acetyl derivative	$OAc.C_6H_4CH_2.CHCl_2$	Oil	190°/50 m. m.	Cl.30.6	Cl,30.5
5. Benzoyl derivative	$OBz.C_6H_4CH_2.CHCl_2$	Plates	114°	Cl,23.9	Cl,24.1
6. Methoxy derivative	$OMe.C_6H_4.CH_2.CHCl_2$	Liquid	187°/30 m. m.	Cl,34.8	Cl,34.6
7. 4-methoxy-ββ-dichloro-α-methoxy ethylbenzene.	$OMe.C_6H_4.CH(OMe)CHCl_2$	Liquid	181°/50 m. m.	Cl,29.9	Cl,30.2
Derivatives of 2 : 4-dihydroxy-β β β-trichloro- α - hydroxy-ethylbenzene.					
8. Tri-acetoxy	$(OAc)_2C_6H_3.CH(OAc)CCl_3$	Thin plates	132°	Cl.27.7	Cl,27.7
9. Tri-benzoyloxy	$(OBz)_2C_6H_3CH(OBz)CCl_3$	Rectangular plates.	142°	Cl,18.5	Cl,18.7
10. Tri-methoxy	$(OMe)_2C_6H_3CH(OMe)CCl_3$	Feathery needles	126°	Cl,35.4	Cl,35.5
Reduction product of triacetoxy above.					
11. Di-acetoxy	$(OAc)_2C_6H_3CH_2.CHCl_2$	Small needles.	67°	Cl,24.2	Cl,24.4
Derivatives of 2:4 dihydroxy-1:5-di-(β β β-trichloro-α-hydroxyethyl)benzene.					
12. Condensation product.	$(OH)_2.C_6H_2[CH(OH)CCl_3]_2$	Long needles	172°	Cl,52.4	Cl,52.6
13. Tetra-acetoxy	$(OAc)_2C_6H_2[CH(OAc)CCl_3]_2$	Thin needles	192°	Cl,37.0	Cl,37.2
14. Tetra-benzoyloxy	$(OBz)_2C_6H_2[CH(OBz)CCl_3]_2$	Rectangular plates.	190°	Cl,25.7	Cl,25.9

Name	Formula	Crystalline nature	m. p.	Analysis	
				found	requir-ed
Reduction products of tetra-acetoxy and tetra-benzoyloxy above.					
15. Di-acetoxy	$(OAc)_2C_6H_2[CH_2.CHCl_2]_2$	Small needles	112°	Cl,36.7	Cl,36.6
16. Di-benzoyloxy	$(OBz)_2C_6H_2[CH_2.CHCl_2]_2$	Rectangular plates.	138°	Cl,27.6	Cl,27.7
17. Di-methoxy	$(OMe)_2C_6H_3\text{-}CH(OMe)CCl_3$	Oil	220°/10 m. m.	Cl,35.3	Cl,35.5
18. Potassium salt.	$\begin{smallmatrix}OK\\OMe\end{smallmatrix}\!>C_6H_3.CH_2.CHCl_2$	...	79°	K,15.1	K,15.1
19. Acetyl derivative	$\begin{smallmatrix}OAc\\OMe\end{smallmatrix}\!>C_6H_3.CH_2.CHCl_2$	Plates.	75°	Cl,27.1	Cl,27.0
20. Benzoyl-derivative	$\begin{smallmatrix}OBz\\OMe\end{smallmatrix}\!>C_6H_3.CH_2.CHCl_2$	White plates	95°	Cl,21.8	Cl,21.8
21. Methoxy derivative	$(OMe)_2C_6H_3CH_2.CHCl_2$	Thick liquid (pleasant odour)	197°/50 m. m.	Cl,30.1	Cl,30.2
22. 4:5-dimethoxy ββ-dichloro-α-methoxyethyl-benzene	$(OMe)_2C_6H_3.CH\text{-}(OMe)CHCl_2$	Light oil	140°/5 m. m.	Cl,26.6	Cl,26.8
Derivatives of 2-hydroxy-5-methyl-β β β-trichloro-α-hydroxy-ethyl-benzene.					
23. Di-acetoxy	$\begin{smallmatrix}OAc\\CH_3\end{smallmatrix}\!>C_6H_3.CH(OAc)CCl_3$	White needles	106°	Cl,31.3	Cl,31.4
24. Di-benzoyloxy	$\begin{smallmatrix}OBz\\CH_3\end{smallmatrix}\!>C_6H_3.CH(OBz)CCl_3$	Rectangular plates.	139°	Cl,22.9	Cl,22.9
25. Di-methoxy	$\begin{smallmatrix}OMe\\CH_3\end{smallmatrix}\!>C_6H_3.CH(OMe)CCl_3$	Needles	104°	Cl,37.5	Cl,37.6

[*Received July 28, 1937.*]

A NOTE ON THE REDUCTION OF SOME DERIVATIVES OF ANHYDRO-2-βββ-TRICHLORO-α-HYDROXYETHOXY-1-βββ-TRICHLORO-α-HYDROXY-ETHYL-BENZENE

By

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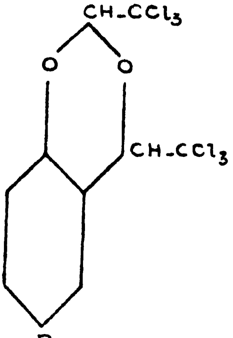
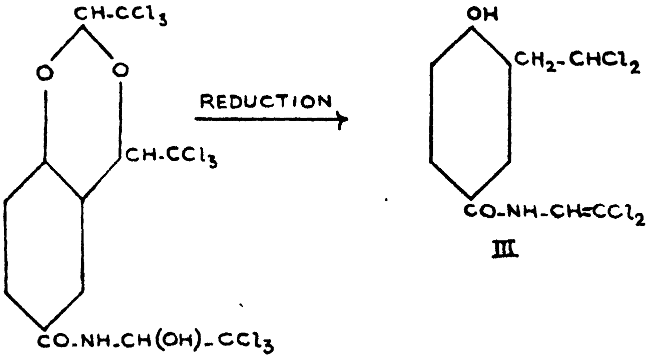
Chattaway and Prats (*J. C. S.*, 1927, 688), and Chattaway and Morris (*J. C. S.*, 1927, 2017), prepared anhydro-5-carbamyl-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethyl-benzene (I ; R = $CONH_2$) and a similar sulphonamide (I ; R = SO_2NH_2).



I

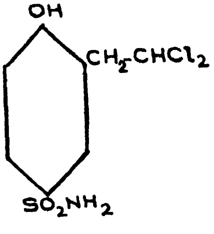
(I ; R = $CONH_2$) has now been condensed with chloral to give (II), which yields (III) on reduction with zinc and acetic acid.



III

II

The sulphonamide ($I : R = SO_2NH_2$) on reduction with zinc and acetic acid gave (IV).



IV

EXPERIMENTAL

Anhydro-5-βββ-trichloro-α-hydroxyethyl-carbamyl-2- βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethyl-benzene. (II)

A mixture of the amide (I ; R $CONH_2$) (20 g.) chloral (excess) and a few drops of conc. sulphuric acid, was heated at 100° for half an hour. The product (24 g.) was washed with water and recrystallised from acetone : needles : m.p. 168°.

(Found Cl, 56·6 ; $C_{13}H_8O_4NCl_9$ requires Cl, 56·9%).

The acetyl derivative of the above chloral-amide (acetic anhydride and two drops of conc. Sulphuric acid) crystallised from benzene. m.p. 220-222°.

(Found Cl, 53·0 ; $Cl_{15}H_{10}O_5NCl_9$ requires Cl, 53·0%).

2-*hydroxy*-5-*ββ-dichloro-vinylcarbamyl- ββ-dichloro-ethylbenzene.* (III).

Zinc dust (5 g.) was gradually added to a mechanically shaken solution of the chloral-amide (5g.) in acetic acid (40 cc.) ; the mixture was finally warmed on a water-bath to complete the reduction. Zinc acetate was filtered off and the filtrate neutralised with sodium carbonate and extracted with ether. The solid (1·5g.) obtained on the removal of the ether crystallised from a mixture of benzene and alcohol ; m.p. 150°-152°. The substance is soluble in alkali and gives a violet colour with ferric chloride. (Found : Cl, 42·9 ; $C_{11}H_9O_2NCl_4$ requires Cl, 43·2%).

The acetyl derivative of the reduction product crystallised from alcohol in needles ; m.p. 155°-56° (Found : Cl, 38·0 ; $C_{18}H_{11}O_3NCl_4$ requires Cl, 38·3%).

Anhydro-2-βββ-trichloro-α-hydroxyethoxy-1- βββ-trichloro-α-hydroxyethyl-benzene-5-sulphonic acid and its amide were prepared according to Chattaway and Morris (*J. C. S.*, 1927, 2014 and 2017).

Sodium salt of the above acid crystallises from water in needles (Found : Na, 4·3 ; H_2O, 10·2 ; $C_{10}H_5O_5Cl_6SNa$, $3H_2O$ requires Na, 4·4 and H_2O, 10·2%).

The potassium salt crystallises from water in ocicular tufts (Found : K, 7·5 H_2O, 3·5 ; $C_{10}H_5O_5Cl_6SK$,H_2O requires K, 7·7% and H_2O, 3·5%).

The calcium salt is prepared by adding calcium chloride solution to the ammonium salt solution. It separates from water in clusters of needles with four molecules of water (Found : Ca, 4·1 ; H_2O, 7·7 ; $C_{20}H_{10}O_{10}Cl_{12}S_2Ca$, $4H_2O$ requires Ca, 4·1 and H_2O, 7·1%).

4-hydroxy-3-ββ-dichloroethylbenzene-sulphonamide (IV).

Zinc dust (5g.) was gradually added to a mechanically shaken solution of the sulphon-amide (I ; $R = SO_2NH_2$) (5g.) in acetic acid (40 cc.). The reduction was complete within four hours. On neutralising the liquid with sodium carbonate solution and extracting with ether, a solid was obtained which crystallised from water in feathery needles ; m.p. 181°-184° (Found : Cl, 26·2 ; $C_8H_9O_3NSCl_2$ requires Cl, 26·3%).

The acetyl derivative crystallised from alcohol in needles : m.p. 140° (Found : Cl, 22·7 ; $C_{10}H_{11}O_4NSCl_2$ requires Cl, 22·8%).

Anhydro-2-βββ-trichloro-α-hydroxyethoxy-1- βββ-trichloro-α-hydroxyethylbenzene-5-βββ-trichloro-α-hydroxyethyl-sulphonamide.

A mixture of the sulphonamide (I ; $R = SO_2NH_2$) (5g.) chloral (3 g.) and two drops of con. H_2SO_4 was heated on a water bath for half an hour. The product after being washed with water crystallised from alcohol in needles ; m.p. 194°-195° (Found : Cl, 53·5 ; $C_{12}H_8O_5NSCl_9$ requires Cl, 53·4%).

The acetyl derivative crystallised from benzene in feathery needles ; m.p. 159°. (Found Cl, 49·6 ; $C_{14}H_{10}O_6NSCl_9$ requires Cl, 49·9%).

[*Received July 31, 1937*].

STUDIES IN CHLORAL-AMIDES—PART IV. REACTIVITY OF α-OH GROUP IN CHLORAL-NITRO-SALICYLAMIDES.

By

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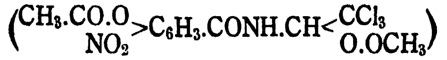
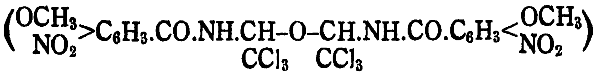
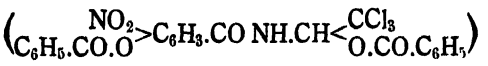
In continuation of nitration of chloral-salicylamide (Studies in chloral-amides, Part II, *J. Ind. Chem. Soc.*), the reactivity of the α-OH group in chloral-nitro-salicylamides has been studied. It can be substituted by various groups such as acetoxy-(O. CO. CH_3) methoxy (O. CH_3), and benzoyloxy (O. CO. C_6H_5).

Acetic anhydride when used, with little sulphuric acid yields a diacetoxy derivative  $\left(\genfrac{}{}{0pt}{}{CH_3.CO.O}{NO_2}{>}C_6H_3.CONH.CH{<}\genfrac{}{}{0pt}{}{CCl_3}{O.OCH_3}\right)$ of the various chloral-nitro-salicylamides, wherein the nuclear hydroxy group and the α-OH group in side chain are both simultaneously acetylated. Unlike that in aspirin, the nuclear acetoxy group in these acetylated Chloral-nitro-salicylamides is found to be more stable. When used in an alkaline medium, it causes an anhydro formation

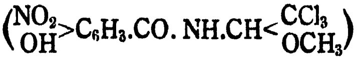


$$\left(\genfrac{}{}{0pt}{}{OCH_3}{NO_2}{>}C_6H_3.CO.NH.\underset{CCl_3}{CH}\text{–}O\text{–}\underset{CCl_3}{CH}.NH.CO.C_6H_3{<}\genfrac{}{}{0pt}{}{OCH_3}{NO_2}\right)$$

With benzoyl-chloride, in sodium hydroxide solution dibenzoyl



$$\left(\genfrac{}{}{0pt}{}{NO_2}{C_6H_5.CO.O}{>}C_6H_3.CO\ NH.CH{<}\genfrac{}{}{0pt}{}{CCl_3}{O.CO.C_6H_5}\right)$$

derivatives are obtained, while dimethyl sulphate in alkaline medium gives only α-methoxy derivatives  $\left(\genfrac{}{}{0pt}{}{NO_2}{OH}{>}C_6H_3.CO.\ NH.CH{<}\genfrac{}{}{0pt}{}{CCl_3}{OCH_3}\right)$ leaving the nuclear hydroxy group unmethylated.

Chloral 3:5-dinitro-2-methoxy-benzamide when similarly treated with benzoyl chloride, gives a dibenzoyloxy compound, the nuclear-O. CH_3 is probably hydrolysed (by NaOH) to-OH, which is further benzoylated ; while in methylation of the same with the dimethyl sulphate in an alkaline medium, the nuclear methoxy is similarly hydrolysed, but not remethylated, thus giving α-methoxy chloral 3 : 5 dinitro-salicylamide. This behaviour of the methoxy group is similar to that in 3 : 5-dinitro-2-methoxy-benzoic acid ; Hirwe and (Miss)

Gavankar (Proc. Ind. Acad. Sci. 1937, 5, 377). The accumulation of more negative groups makes the ether ($-OCH_3$) less stable.

It is interesting to note that in the case of nitro-chloral-salicylamides the chloral-amide linking is much more stable towards alkali than in other chloral-amides of salicylic acid.

EXPERIMENTAL

Methylation :—(The nuclear methoxy group—with the increase in the number of negative groups becomes usually unstable and is hydrolysed under conditions of experiment, not being remethylated. Thus the only hydroxy group that was methylated was the α-hydroxy group in the side chain).

Required quantity of methyl sulphate was added to the chloral-nitro-salicylamide in sodium hydroxide solution (10%) at 25°-30° and then kept overnight. On acidifying the reaction mixture, the required α-methoxy compound was obtained either as solid or a paste, which was further treated to get a solid.

Benzoylation :—Benzoylation of either chloral-nitro-salicylamides or chloral-nitro-2-methoxy-benzamides gave α-benzoyloxy chloral-nitro-2-benzoyloxy-benzamides. The 2-methoxy group in chloral-3-nitro-2-methoxy-benzamide was hydrolysed and then benzoylated under the conditions of experiments.

Method :—Required quantity of benzoyl chloride was added to chloral-nitro-salicylamide or chloral-nitro-2-methoxy-benzamide in sodium hydroxide solution (10%) in cold. The reaction mixture on keeping over-night was acidified, when a solid or a paste, which was further treated to get a solid, was obtained. The yields are poor.

Anhydro derivatives :—These compounds are obtained by the elimination of a molecule of water from the two α-hydroxy groups of the two molecules and thus linking them together through oxygen.

Method :—Required quantity of acetic anhydride was added to a solution of chloral-nitro-2-methoxy-benzamide in sodium hydroxide (10%) in cold. This was kept for 12 hours and then acidified when the required compound was obtained.

Acetylation :—Nuclear and side chain hydroxy group was simultaneously acetylated by the usual method. The compound to be acetylated, was warmed with acetic anhydride with few drops of sulphuric acid. On diluting the reaction mixture, a solid separated.

α-methoxy-chloral-3-nitro-2-hydroxy-benzamide :— Crystallised from alcohol in yellow rectangular plates m. p. 114° (Found Cl, 31·0; $C_{10}H_9O_5N_2Cl_3$, requires Cl, 31·0 per cent).

α-methoxy-chloral-5-bromo-3-nitro-2-hydroxy-benzamide :— The sticky mass separated was solidified by keeping in a freezing mixture. It crystallised from acetic acid in yellow granules m.p. 115-116° (Found : Halide, 145·4, $C_{10}H_2O_5N_2Cl_2Br$ requires Halide, 146·4 per cent).

α-acetoxy-chloral-3-nitro-2-acetoxy-benzamide :—Crystallised from ethyl alcohol in fine white needles m.p. = 151-152°. (Found Cl, 25·8 ; $C_{13}H_{11}O_7N_2Cl_3$ requires Cl, 25·8 per cent).

α-acetoxy-chloral-5-bromo-3-nitro-2-acetoxy-benzamide :—Crystallised from ethyl alcohol in white needles m. p. 168° (Found : Halide, 124·8, $C_{13}H_{10}O_7N_2Cl_3$ Br requires Halide, 125 6 per cent).

α-methoxy-chloral-3 :5-dinitro-2-hydroxy-benzamide :—

(1) From chloral-3 : 5-dinitro-2-hydroxy-benzamide :—Crystallized from methyl alcohol in yellow rectangular plates m.p. = 172° (Found Cl, 27·5 ; C, 31·1 ; H, 2·1 ; $C_{10}H_8O_7N_3Cl_3$ requires Cl, 27·4 ; C, 30·9 ; H, 2·1, per cent.)

(2) From chloral-3:5-dinitro-2-methoxy-benzamide m.p. 172° mixed m.p. with (1) is 172°C.

α-benzoyloxy-chloral-3 :5-dinitro-2-benzoyloxy-benzamide :—

(1) From chloral-3 : 5-dinitro-2-hydroxy-benzamide :—Crystallised from benzene in white granules m.p. 196-197° (Found : Cl, 18·1, $C_{23}H_{14}O_9Cl_3$ requires Cl, 18·3 per cent.)

(2) From chloral-3 : 5-dinitro-2-methoxy-benzamide : crystallised from benzene in white granules m.p. 196-197° mixed m.p. with (1) is 196-197° (Found : Cl, 18·4, $C_{23}H_{14}O_9N_3Cl_3$ requires Cl, 18·3 per cent.)

α-acetoxy-chloral-5-nitro-2-methoxy-benzamide :— Crystallised from ethyl alcohol in white needles m.p. = 168-169° (Found : Cl, 27·6, $C_{12}H_{11}O_6N_2Cl_3$ requires Cl, 27·6 per cent.)

α - anhydro-di(chloral-5-nitro-2-methoxy-benzamide) :—Crystallised from glacial acetic acid in fine white needles m.p. 207-208° (Found : Cl, 31·6, $C_{20}H_{16}O_9N_4Cl_6$ requires Cl, 31·5 per cent.)

α-benzoyloxy-chloral-5-nitro-2-methoxy-benzamide :— Crystallised from glacial acetic acid in white granules m.p. = 175-176° (Found : Cl, 24·1, $C_{17}H_{13}O_6N_2Cl_3$ requires Cl, 23·8 per cent.)

α-methoxy-chloral-5-nitro-2-methoxy-benzamide :— Crystallised from ethyl alcohol in white cubic plates m.p. 144° (Found : Cl, 29·5, $C_{11}H_{11}O_6N_2Cl_3$ requires Cl, 29·8 per. cent.)

α-methoxy-chloral-3-nitro-2-methoxy-Benzamide :— Crystallised from methyl alcohol in yellow rectangular plates m.p. = 104-105° (Found : Cl, 29·5, $C_{11}H_{11}O_5N_2Cl_3$ requires Cl, 29·8 per. cent.)

α-acetoxy-chloral-3-nitro-2-methoxy-benzamide :— Crystallised from methyl alcohol in white needles m.p. = 94-95° (Found Cl, 27·8, $C_{12}H_{11}O_6N_2Cl_3$ requires Cl, 27·6 per cent).

α-acetoxy-chloral-3 : 5-dinitro-2-methoxy benzamide :— Crystallised from ethyl alcohol in yellow cubic plates m.p. = 172° (Found : Cl, 27·61 $C_{10}H_8O_7N_3Cl_3$ requires Cl, 27·4 per cent.)

α-anhydro-di(chloral-3-nitro-2-methoxy-benzamide) :— Crystallised from methyl alcohol in white silky needles m.p.—153-154° (Found : Cl, 32·1, $C_{20}H_{16}O_9N_4Cl_6$ requires Cl, 31·9 per cent).

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DERIVATIVES OF N-PHENYLBENZAMIDINE : PART I.

By

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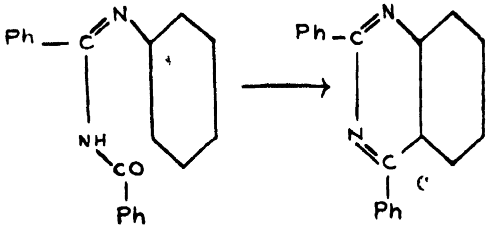
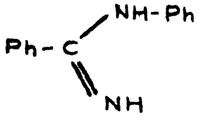
In extension of the previous work on synthesis of heterocyclic nitrogen compounds from anilideimidochlorides (*J.*, 1936, 428, 431; 1937, 867), it was contemplated to synthesise 2 : 4 diphenylquinazoline by dehydration of the benzoyl derivative of N-phenylbenzamidine.

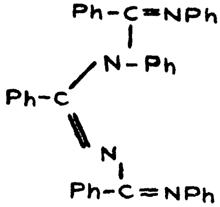


N-Phenylbenzamidine (I), required for this work was first prepared by shaking together a mixture of petroleum ether solution of benzanilideimido-chloride and aqueous ammonia Lossen, *Annalen*, 1891, 265, 138), but a poor yield was obtained. Pyman (*J.*, 1923, 3365) reported also a yield of 16 gms. only from 100 gms. of benzanilide. Various modifications of this method were tried and ultimately an improved method has been worked out which gives a 75% yield of the amidine. The improved method consists in adding an ethereal solution of the imidochloride to a concentrated methyl-alcoholic solution of a large excess of ammonia. With less ammonia a second compound m.p. 176-178° is obtained also, which renders the purification of (I) difficult and reduces its yield. The bye-product m.p. 176-178° was found to be produced by the further condensation of (I) with 2 mols. of the imidochloride and this was confirmed by its synthesis from (I) and benzanilide imidochloride. The compound m.p. 176-178° has been assigned the constitution (II), derived from formula (I), although it may have the less probable alternative structure (II A) derived from (IA), the tautomeric form of (I). The constitution (II) has been assigned on the following grounds :—(1) In many of its reactions N-phenylbenzamidine reacts in the form (I)e.g. with phenylisocyanate, it gives N-phenyl-N′-phenyl-carbamyl benzamidine of established constitution (Wheeler, *J. Am. Chem. Soc.*, 1901, 23, 223;

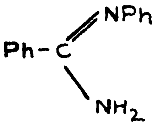
Wheeler and Sanders, *J. Am. Chem. Soc.*, 1900, *22* 365), (2) In benzoylation, there is a strong tendency for the formation of the diderivative even with excess of amidine, which would not be the case if it reacted in form (IA), in which case the second hydrogen atom attached to the same nitrogen atom would be difficult to replace.



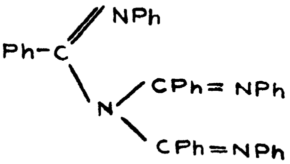
I



II

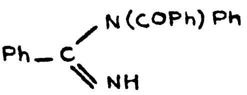


IA

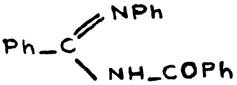


IIA

Wheeler, Johnson and McFarland (*J. Am. Chem. Soc.*, 1903, 793) benzoylated (I) in cold ether solution by benzoyl chloride and obtained a compound m.p. 95-97° which on crystallisation from alcohol gave a compound m.p. 143°. The compound m.p. 95-97° was assigned the constitution (III) as it gave benzanilide on hydrolysis. The compound m.p. 143° was given the formula (IV) as it gave dibenzamide on hydrolysis and no benzanilide. We have repeated this work and have confirmed it. The monobenzoyl derivative (IV), m.p. 143° required for synthesis of 2 : 4-diphenyl quinazoline was thus prepared; although in poor yield. In order to get a better yield various other methods were tried. Benzoylation in pyridine solution with 1·2 mols. of benzoyl chloride gave a dibenzoyl derivative. Benzoylation with ½ mol. of benzoyl chloride ultimately gave dibenzamide probably formed by the hydrolysis of the monobenzoyl derivative.

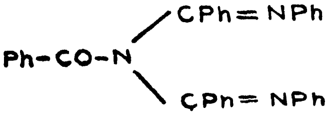


III



IV

As the yield of (IV) by the method of the American workers was poor, it was thought of interest to see whether (IV) could be obtained by the direct condensation of benzanilide imidochloride with benzamide. An attempt to condense benzamide with the imidochloride in the presence of diethylaniline or pyridine was unsuccessful, although benzamide condenses with benzoyl chloride in presence of pyridine (Titherley, *J.*, 1904, *85*, 1679). The condensation of sodium derivative of benzamide with the imidochloride under different conditions gave diphenylbenzamidine m. p. 143° on a di-condensation product of the imidochloride with benzamide of the probable formula (V).



V

Various attempts were made to cyclise (IV) to 2 : 4 diphenylquinazoline by the action of heat, phosphoryl chloride, sulphuric acid and phosphoric anhydride, but in no case could the expected cyclisation be brought about.

EXPERIMENTAL

Improved Method for the preparation of N-phenyl-benzamidine :

Benzanilideimidochloride (50 g.) dissolved in dry ether was gradually added to a saturated solution of ammonia in methyl alcohol (500 c.c.), kept cooled by a freezing mixture. After standing overnight, methyl alcohol and ether were distilled off, ice added to the pasty residue which was subsequently extracted with warm dilute HCl The solution was filtered from a small quantity of insoluble matter, and cautiously made alkaline with dilute NaOH with cooling by ice. The colourless granular precipitate was collected, washed with water and after drying, crystallised from a mixture of dry benzene and dry petroleum ether (b. p. 65-95°) in colourless clusters of needles m.p. 115-117° (Lossen, (*loc. cit.*)—m.p. 112° ; Bernthsen A, *184*, 348—m.p. 111-112°). Yield—37 gms. (Found : N, 14·1. Calc. for $C_{13}H_{12}N_2$, N, 14·2 per cent).

Formation of (II).

(*i*) When the previous experiment ,was repeated, using only 250 c.c. of methyl alcohol, the reaction mixture on leaving overnight deposited cream coloured prisms m.p. 174°, which on crystallisation from benzene melted at 176-178°. The methyl alcoholic mother-liquor on working up gave a mixture of (I) and (II), which was difficult to separate into its constituents (Found : N, 10·2 $C_{39}H_{30}N_4$ requires N, 10·0 per cent).

(*ii*) To N-phenylbenzamidine (2 mol.) dissolved in the required quantity of methyl alcohol was added to an ether solution of the imidochloride (1 mol.). On allowing the mixture to stand overnight, a cream coloured crystalline solid separated, which after crystallisation from benzene melted at 176-178°, and was found by mixed m.p. to be identical in all respects with the product obtained by the previous method.

Hydrochloride.

The base m.p. 176-178° was dissolved in dry benzene and saturated with dry HCl. After evaporation of benzene the residue was treated with petroleum ether (b. p. 60-90°), and the insoluble hydrochloride m.p. 240-245°, crystallised from glacial acetic acid in colourless prisms, m.p. 244-246° (Found : N, 98 ; $C_{39}H_{30}N_4$, HCl requires N, 9·5 per cent).

Dibenzoyl derivative of N-phenylbenzamidine.—

Benzoyl chloride (1·2 mols.) was added to the amidine (1 mol.) dissolved in pyridine, and the mixture left in the frigidaire overnight. The mixture was poured into dilute H_2SO_4, and the resulting pasty mass, which solidified in the frigidaire, crystallised from alcohol in colourless fine needles. The *dibenzoyl derivative* had m.p. 143°, which was much depressed by admixture with the monobenzoyl derivative (IV) m.p. 143° (Found : C, 79·9 ; H, 4·8 ; N, 6·8. $C_{27}H_{20}O_2N_2$ requires C, 80·1 ; H, 4·9 ; N, 6·9 per cent).

If the quantity of benzoyl chloride in the above experiment was ½ mol., the product obtained had m.p. 148-149° and was identified as dibenzamide by direct comparison (Found : C, 74·5 ; H, 5·0 ; N, N. 6·2, Calc. for $C_{14}H_{11}O_2N$, C, 74·6 ; H, 5·0 ; N, 6·2 per cent.)

Reaction of the sodium derivative of benzamide with benzanilide-imidochloride.—

(*i*) Benzamide (1·25 mol.) dissolved in dry ether was slowly added to a mixture of pulverised sodium (1·25 atom) and dry ether. After keeping overnight, an ethereal solution of benzanilide-imidochloride (1 mol.) was added, and the mixture refluxed for 5 hrs. Water was added and benzanilide which separated was filtered off. Evaporation of ether fro[illegible] ethereal layer gave a solid, which crystallised from alcohol in [illegible]es m.p. 143°, which was not depressed by admixture with an authentic specimen of diphenylbenzamidine (Found : C, 83·0, H, 5·1 ; N, 10·1. Calc. for $C_{19}H_{16}N_2$, C, 83·8, H, 5·8 ; N, 10·2, per cent).

(*ii*) Imidochloride (1 mol.) dissolved in dry ether was added to the sodium derivative of benzamide (2 mols.) as before. Ether was allowed to evaporate off, and dry toluene added, and the mixture was refluxed for 5 hours. After addition of water to the cooled mixture, the toluene layer was separated and toluene distilled off under reduced pressure. The residue crystallised from alcohol in colourless prisms m.p. 171-172°. The *compound* has the probable constitution (V) (Found : C, 81·9, H, 5·2. $C_{38}H_{25}ON_3$ requires C, 81·7, H, 5·1 per cent).

Attempted cyclisation of (IV).

(*i*) (IV) was kept at 200°C for some hrs. On crystallisation of the product, only benzanilide probably produced by hydrolysis was obtained.

(*ii*) (IV) when boiled with phosphoryl chloride for several hours also ultimately gave benzanilide.

(*iii*) The benzoyl derivative dissolved in xylene was boiled with phosphoric anhydride for some hours. Only unaltered substance m.p. 140-143° was finally obtained.

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PHOSPHORYL CHLORIDE AS A CONDENSING AGENT IN THE PREPARATION OF AMIDINES FROM ACYLAMINES

By

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There are generally two available methods for the preparation of amidines from acylamines and amines :—

(i) the method of Hill and Cox (*J. Am. Chem. Soc.*, 1926, *48*, 3214) in which the condensation is brought about in the presence of phosphorous pentachloride, and (ii) Hoffmann's method, in which phosphorous trichloride is used as the condensing agent (Z., 1866, 161 ; Sen and Ray, *J.*, 1926, 646). During the course of the work on the synthesis of diaryl-cinnamidines from cinnamanilides (Sidiki and Shah—under publication), it was considered worth while to investigate the use of phosphoryl chloride as a condensing agent, as the yields with phosphorous trichloride were not good enough and the products difficult to purify. The use of phosphoryl chloride, which does not appear to have been used previously for this purpose, gave a much better yield of diphenylcinnamidine, the yield with phosphoryl chloride being 76%, and that with phosphorous trichloride being only 49%. The reagent was found to be an efficient condensing agent in the preparation or known typical amidines like diphenylbenzamidine and diphenyl-acetamidine. Further, diphenylcrotonamidine, which could not be prepared by the methods of Hill and Cox, or Hoffmann, was readily obtained by this method.

EXPERIMENTAL

Condensation of Cinnamanilide with aniline in the presence of phosphoryl chloride :— A number of experiments under different conditions were tried and the following experimental conditions gave the best results. To a mixture of cinnamanilide (1 mol : 5 g.) and aniline (1 mol : 2·1 g.) $POCl_3$ (35 g.) was added, and the mixture protected from moisture, heated for 5 hours in an oil bath at 140-150°, till the evolution of HCl was negligible. The cooled mixture was poured into ice cold water, when a yellow solid hydrochloride ([illegible]5 g.) separated. The hydrochloride on boiling with concentrated ammonia give ***diphenyl-cinnamidine*** which crystallised from alcohol in yellow needles (5·45 g.). M.P. 123°, and mixed m.p. with the product obtained by using PCl_3 (Sidiki and Shah, *loc. cit.*) showed no depression. (Found : N, 9·6. $C_{21}H_{18}N_2$ requires N, 9·4 per cent.).

Diphenylacetamidine and diphenylbenzamidine were prepared using the same experimental conditions from acetanilide and benzanilide respectively in yields of 84% and 80% respectively. The effect of using P_2O_5, $KHCO_3$, $ZnCl_2$, along with $POCl_3$ in such condensations was also investigated, but it was found that the yield was not improved and the products were more impure.

Diphenyl crotonamidine—The condensation of crotonanilide (*Authenreith, Ber.*. 1905, *38,* 2566) and aniline could not be successfully brought about in the presence of PCl_5 or PCl_3, the products in both cases being uncrystallisable and pasty. The amidine was readily obtained with phosphoryl chloride. A mixture of crotonanilide (4·6 g.), aniline (2·2 g.) and $POCl_3$ (30 g.) was heated at 130-140° in an oil bath for 3 hours. The cooled mixture, when poured into water gave a pasty insoluble hydrochloride. The hydrochloride was dissolved in hot dilute HCl, and the amidine precipitated by alkali extracted with ether. The residue from ether extract, on crystallisation from hot alcohol, gave colourless needles of *diphenyl crotonamidine* m.p. 85° (Found : N, 11·7. $C_{16}H_{16}N_2$ requires N, 11·9 per cent). It is sparingly soluble in hot water, and readily in hot dilute HCl. It is very soluble in the usual organic solvents.

The authors are grateful to the University of Bombay for a research grant.

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PRODUCTION OF TERPINEOL FROM PINENE

By

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This paper describes the results of an investigation on the production of terpineol from pinene. A systematic study of possible processes has been made and an improved process which may be worth investigation on a semi-technical scale has been developed. The stages involved are :

Pinene → Terpin hydrate → Terpineol.

The best yields now obtained for the above stages are :

Pinene → Terpin hydrate 40·3%

Terpin hydrate → Terpineol 89·4%

This gives an over-all yield of 36%.

EXPERIMENTAL

The turpentine (American turpentine employed) to be used as a source of pinene was distilled and the pinene fraction (158-160°) collected.

Pinene → Terpin Hydrate.

As a result of systematic investigation on the following variables (1) temperature (2) strength of H_2SO_4 (3) quantity of H_2SO_4 (4) emulsifiers and (5) time of shaking, the optimum conditions were found to be as follows :—

Pinene (1 part) and sulphuric acid (22-25% ; 1·75 parts) are shaken vigorously for 35 to 40 hours with gelatin 2-2·5%, which acts as an emulsifying agent, when sandy crystals of terpin hydrate are copiously formed. At the outset a few crystals of terpin hydrate are added to act as nucleii for crystallisation. The liquid is filtered to remove the terpin hydrate (0·44 to 0·45 parts) and the filtrate is again shaken for about 5 to 6 hours with dilute sulphuric acid (22-25% ; 0·25 parts). The solid now formed is collected and the whole product is washed with water and treated with dilute sodium carbonate solution, filtered and dried. Yield of terpin hydrate, 40·3% of the theoretical ; m.p. 116-117° ; m.p. of pure product 117°. The use of emulsifying agents such as gelatin is new. It considerably accelerates the reaction.

Terpin Hydrate → Terineol.

A number of acids were examined and oxalic acid proved to be most satisfactory. The optimum conditions were found to be as follows :

Terpin hydrate is boiled under reflux for 6 to 7 hours with twice its weight of 0·5% oxalic acid solution (*Aschan, Chem. Zentr.* 1919, *1*, 284). The yellow upper oily layer containing terpineol is separated, the fraction boiling at 200-214° being collected. Yield 89·4% of the theoretical.

The following reactions were also examined by the methods given in the literature but no successful result was obtained.

Pinene → Terpineol.

Pinene → Terpineol esters.

Our best thanks are due to the University of Bombay for a grant to one of us (B.G.S.A.) towards the expense of the research.

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STUDY OF SOME PHYSICAL PROPERTIES OF COMMERCIAL GUMS

By

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The study of physical properties such as viscosity, pH value, surface tension, protective power, etc. of substances like glue and gelatin has made it possible to utilize them in a number of industries—photography, sizing, binding, food-stuffs and pharmaceutical preparations.

The compounds of colloidal carbohydrate acidic bodies, occurring as exudates on plants, resemble glue and gelatin. Of the many gums available in the Indian market, the physical properties of only gum Acacia arabica seem to have been studied at some length. Pearce and Leary (*J. Phys. Chem.*, *28*, 51, 1924) showed that the hydrolysis of methyl acetate by hydrochloric acid was retarded in the presence of gum Acacia arabica. Thomas and Murray (*J. Phys. Chem.* *32*, 676, 1928.) studied the pH and viscosity relationship of gum Acacia arabica. Taft and Bingham (*J. Phys Chem.*, *36*, 2338, 1932) substituted Gum Acacia as an addition compound for gelatin while studying the electrodeposition of copper from copper sulphate. Gum Acacia on account of its similarity in properties with gelatin is used now by calico-printers.

Besides gum Acacia arabica there are many gums, whose physical properties do not seem to have been investigated at all. With a view to see if by the study of the physical properties of certain gums available in the Indian market, some industrial application for them could be found, an attempt has been made in the present investigation to study the charge, protective power, viscosity, pH value, refractive index, surface tension of colloidal solutions of gums whose habitat, appearance and solubility are tabulated below.

Indian Name.	Botanical Name.	Appearance.	Solubility.	Habitat.
Gond Kikar	Acacia arabica	Glistening, transparent, round ovoid tears; colour varies from pale yellow to reddish brown.	Completely soluble in water.	It is obtained from Acacia arabica at various places in the Punjab: Rohtak, Ambala, Lahore, Gujrat, Shahpur, Jullunder, Kangra, Amritsar,
Gond Khair	Acacia catechu	Round ovoid shaped crystals white to greenish tinge.	Completely soluble in water.	It is obtained from the bark of "Catechu" when wounded, in the neighbouring territories of Hissar district, Gurgoan and Mewatti hills.
Isab Ghol	Plantago ispaghula	Small oval grey seeds	Swells up in water forming a demulcent mucelage.	It is grown all over India and occurs wild in Punjab plains and low hills.
Gond Katira	Cochlospermum gossypium (False Tragacanth)	Semi-transparent white gum in striated pieces, very much twisted and contorted.	Swells up in water forming a viscous mass.	It is imported from Garhwal, Kumaon, Hardwar, Sub-Himalayan Hills, Frontier Hills of N. W. Province.
Gond Ushak	Dorema ammoniacum	Pale yellow externally and white within. It is available in the form of small globular tears agglutinated together.	It is partially soluble in water, when ground up in a mortar with the same, a very fine milky solution is obtained which is bitter in taste.	Dorema ammoniacum occurs in dry plains of N. W. Afghanistan, N. W. Slopes of Hindukush, and parts of Persia.

Indian Name	Botanical Name	Appearance	Solubility	Habitat
Rumi Mastiki.	Pistacia lentiscus.	It occurs as a yellow gum resin in small round semi-transparent tears.	It is insoluble in water and soluble in spirit.	It is obtained from Pistacia lentiscus or P. allantica, which grows on the shores of Levant and parts of Greece, and in the islands of Archipelago. It comes from Turkey but best is said to come from Kabul and Levant and hence called Rumi.
"Bol" Myrrh mekka	Balsamodendron myrrha.	Real Myrrha is dark reddish brown like Gugal in small lumps and bitter in taste.	It is partially soluble in water and ether.	It is produced by Balsamodendron myrrha grown in Arabia. It is exclusively imported from Bombay whence it comes from Arabia.
Alkundaru or Kundar	Boswellia thurifera.	Small pale yellowish to greenish translucent tears.	It is partially soluble in water, ether and alcohol.	It is produced from Boswellia thurifera which grows to a large size in low dry hills of India.

EXPERIMENTAL

Charge on the particles.

2% solution of gum Acacia arabica and 0·5% solution of the other gums were prepared in conductivity water. The sign of the charge of the gum particles was determined by the ordinary U-tube method using platinum electrodes and 110 volts current at 20°C. With the exception of Plantago ispaghula sol, where the particles settled down at the bottom, the rest moved towards the anode, showing that ispaghula particles are neutral, whereas the rest are negatively charged.

Protective Power.

Standard gold solution was prepared by adding 5 c.c. of 1% hydrogen gold chloride to a 500 c.c. boiling conductivity water in a Pyrex flask. 50 c.c. of alcohol was added and the solution on heating for 15-20 minutes became blood red. To 10 c.c. of this cooled standard gold solution different amounts of gum solution were added and the gold number as determined is tabulated below.

Botanical name of the Gum.	*Gold Number*
(Gelatin)	0·0050-0·0125
Gum Acacia catechu	0·0015-0·0025
Gum Balsamodendron myrrha	0·0150-0·0200
Gum Boswellia thurifera	0·0400-0·0500
Gum Acacia arabica	0·0450-0·0500
Gum Plantago ispaghula	0·1250-0·1500
Gum Cochlospermum gossypium	0·2500-0·3000
Gum Dorema ammoniacum	1·0500-1·1500
Gum Pistacia lentiscus	No protective power

Viscosity.

Scarpa's method as modified by Farrow was used. The viscometer along with the guard tube was enclosed in an electrically heated thermostat.

$$\text{Viscosity} = \frac{t_1 \times t_2}{t_1 + t_2} \times k.$$

where t_1 is the time taken to draw up sufficient liquid to fill up the tube upto the top mark through the vertical capillary tube of 0·85 mm. bore and t_2 the time required by this liquid to flow under its own weight, and k is a constant, which was determined by finding out $\frac{t_2 \times t_1}{t_1 + t_2}$ for pure water whose absolute coefficient viscosity at different temperatures is known. Before proceeding with the investigation of the viscosities of the colloidal gum solutions the apparatus was tested by determining the viscosities of the standard liquids such as benzene, toluene, aniline, etc. It was found that the agreement between the experimental and the exact values as given in the table of physical constants was quite satisfactory.

The influence of concentration and temperature on viscosity is plotted in figs. 1 and 2.

The pH value of the various gum solutions at various concentrations and in the presence of sodium acetate was determined by the potentiometric method. The results obtained are graphically represented in Fig. 3.

Refractive index of Gum Acacia arabia and Acacia catechu at different concentrations and at different temperatures was determined by Abbe's refractometer and the results are represented in Figs. 1 and 2.

Surface tension of the gum solutions at different concentrations was observed and the results are plotted in Fig. 1.

SUMMARY AND DISCUSSION

From the study of the physical properties of different gum solutions, we find that

(1) All of them with the exception of Plantago ispaghula are negatively charged and are acidic in nature; Cochlospermum gossypium is the most acidic of all, followed by Acacia catechu and Dorema ammoniacum.

(2) The order of their viscosity is Cochlospermum gossypium > Plantago ispaghula > Acacia catechu > Acacia arabica > Balsamodendron myrrha > Dorema ammoniacum > Pistacia lentiscus.

(3) The order of protective power is Acacia catechu > Balsamodendron myrrha > Boswellia thurifera > Acacia arabica > Plantago ispaghula > Cochlospermum gossypium > Dorema ammoniacum > Pistacia lentiscus.

(4) At higher concentrations Balsamodendron myrrha lowers the surface tension very much followed by Dorema ammoniacum, whereas at lower concentrations the power of lowering the surface tension is reversed. Acacia arabica and Acacia catechu do not affect the surface tension of water.

All the gum sols are negatively charged with the exception of Plantago ispaghula which is neutral. These gums are acidic carbohydrate bodies. Gum arabica has been shown by Thomas and Murray (*J. Phys. Chem.*, 32, 676, 1928) to yield on hydrolysis

the so-called arabic acid. Schematically this can be represented as RCOO-H. This "RCOO" is the colloidal micelle which migrates to the anode. The acidic character of the gums therefore explains the charge on the colloidal micelle.

Colloidal solutions have been classified into two main groups—lyophobic and lyophilic, based upon some of their characteristic properties. The capacity to remain in colloidal state in the presence of electrolytes was the criterion of classification of Perrin and Freundlich. Viscosity and refractive index of the lyophobic sols vary directly with concentration, whereas they increase in the case of lyophilic ones. Surface tension is another property which distinguishes one from the other. Surface tension of most of lyophilic sols such as those of silicic acid, starch and related compounds, do not differ at all or very slightly from that of the dispersion medium, but there are others such as those of proteins, which lower the surface tension appreciably.

None of these properties alone, therefore, can be utilised to classify the sols.

From the viscosity—concentration curve of the gum solution, it is clear that the viscosity of Dorema ammoniacum and Pistacia lentiscus varies directly with the concentration and those of Cochlospermum gossypium, Plantago ispaghula, Acacia catechu and Acacia arabica increase with concentration. But viscosity of Balsamodendron varies directly upto 4% and beyond that it has a tendency to increase with concentration.

Surface tension of water is lowered by Dorema ammoniacum and Balsamodendron whereas it is not affected by Acacia arabica and Acacia catechu.

In general, from the study of these properties, therefore, it may be stated that the behaviour of Acacia catechu, Acacia arabica, Cochlospermum gossypium and Plantago ispaghula is similar to the behaviour of lyophilic colloids while that of Dorema ammoniacum, Pistacia lentiscus and Boswellia thurifera corresponds to that of lyophobic. But Balsamodendron exhibits lyophobic character upto 4% and beyond that it behaves like lyophilic colloids. Study of refractive index, as is clear from Fig. 1 also brings us to the same conclusion.

The viscosity temperature curve of these gum sols, if plotted as in Fig. 2, indicates that in case of Acacia catechu and Acacia arabica, with the rise of temperature the viscosity decreases and the convexity of the curve towards the temperature axis decreases and the curve steepens.

Incidentally the effect of the addition of sodium acetate on pH was studied as well. It was observed that gum Dorema ammoniacum and Balsamodendron required the large amount of sodium acetate to change the pH value 4·8 to 6·0. Greater addition of the electrolyte to bring down the acidity indicates greater adsorptive power of the colloidal particles; Dorema ammoniacum and Balsamodendron, therefore seem to have great adsorptive power.

It is generally believed that viscosity and protective power of a colloid go side by side. Gelatin, glue, albumin, etc. have high viscosity values and are supposed to be very good protective agents. But this generalisation does not hold good in all the gums studied by us. Cochlospermum gossypium and Plantago ispaghula possess the highest viscosity but are very poor protective agents, whereas Balsamodendron and Boswellia thurifera are less viscous but are very good protective agents. Acacia catechu, Pistacia lentiscus and Dorema ammoniacum are the ones in which this generalisation seems to hold good.

It was believed that the low viscosity of Balsamodendron and Boswellia thurifera may be on account of some impurity present in the commercial gums which might be masking their high viscosity but on repeating the experiments with purified samples, similar results were obtained.

CONCLUSION

As a result of the present investigation it appears that the taste, smell, solubility in water, high protective power, acidity and viscosity values would enable us to use Acacia catechu as an adhesive in calico printing and in various food-stuffs and pharamceutical preparations. On account of its very high adsorptive and protective power Balsamodendron can be used as an antidote in cases of poisoning with acids and alkalies. Pistacia lentiscus because of its brittleness, lustre, insolubility in water, solubility in spirit and of lyophobic character can be used in polish liquors. Boswellia thurifera is slightly soluble in water, but is fairly soluble in organic solvents and has very high protective power and can therefore be used for the protection of organic sols. Plantago ispaghula on account of its swelling property and high viscosity can replace agar agar in medicinal uses.

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A COMPARISON OF THE OILS FROM THE LOCAL AND SPANISH VARIETIES OF GROUND-NUT.

By

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During the last decade the Government Departments of Agriculture are advocating the growing of the Spanish variety of groundnut in perference to the Local indigenous variety as the former has certain advantages over the latter. Owing to this the local variety is fast being displaced by the foreign one. This investigation was undertaken to compare the two varieties of ground-nut as to the nature of their oils and proteins. The comparative study of the oils is presented in this paper. Further Jamieson, Baughman and Brauns (*J. A. C. S.* 1921. *43*, 1937.) have analysed the oil from the American grown Spanish variety and it will be interesting to compare it with the oil of the same variety grown in India.

India produces half the world's total output of ground-nut seeds which occupy 29 per cent of the area under cultivation of oilseeds in this country. The oil, which is 50 per cent of the seed, is milled mainly from the indigenous local ghanis—a crude pestle and mortar type crusher.

The cold pressed oil is almost colourless and has a taste not unlike that of the olive oil. It is a typical non-drying oil, hardening at about—7°C. and does not easily turn rancid. In India the oil is mainly used for culinary purposes. It is also used widely as an adulterant for ghee and in that form is more extensively consumed than is apparent. In industry, it is used for soap making, for making vegetable ghee and as a lubricant. It has been recommended as a good substitute for olive oil in medicine.

Description of the two varieties.

The Local or the idigenous variety of the ground-nut has developed out of the Brazilian seed imported long ago. In the plants of this variety the stem creeps along the ground and nuts are formed all along the stem. Also, all the pods do not mature simultaneously. This makes harvesting more difficult. The seed has wrinkles on the body and has a pale red colour. There are usually three seeds per pod.

The Spanish variety is supposed to have been introduced into this country in 1907 from Spain. This is fast replacing the indigenous variety as it has certain advantages. It is upright in habit and the nuts cluster round the roots in bunches. All fruits mature simultaneously. The seeds are small and round. There are two seeds in every pod. The yield per acre as well as the oil content are higher in this variety. Also, the shell content is smaller, being only 20 per cent. as against 24 of the Local variety.

The following table gives the variation as regards the oil content, shell and kernel in the two varieties of ground-nut.

TABLE 1.

	Local	Spanish
Oil	43·06—48·24	44·38—54·34
Shell .. .	21·70—35·62	15·57—29·03
Kernel	65·26—89·20	74 02—84·43

TABLE 2.

Analysis of Ground-nut Pods.

	Local	Spanish
Weight of 100 pods	120·6 gms.	98·25 gms.
Number of seeds per pod (average)	3	2
Ratio of Seed to Shell .	3·22 : 1	4 11 : 1
Oil extractable in Ghani ..	80 percent	90 percent.

TABLE 3.

Analysis of Ground-nut Kernel.

	Local	Spanish
Moisture	3·58	3·64
Ash .. .	2·27	2·36
Crude Fibre	2·38	2·05
Crude Protein (N x 6·25)	35·26	31·88
Ether Extract	46·17	51·08
Carbohydrates (by difference)	10 34	8·99
	100·00	100·00

The main differences between the seeds of the two varieties are the higher oil content and lower shell content of the Spanish variety. The Local variety has already been pointed out to be harder to crack yielding a lower percentage of oil on expression.

EXPERIMENTAL

The pure strains of the two varieties were obtained from the Farm, College of Agriculture, Poona. The oil was cold pressed in a ghani, the seeds being moistened to facilitate the expression. The oil as obtained was opaque and hence was kept for a day to let mucilage and other suspended matter settle and then decanted and filtered. The filtered oil was clear and golden yellow in colour. It was preserved in dark amber coloured bottles in an atmosphere of carbon dioxide.

The physical and chemical constants were then determined in the two varieties of oils by methods recommended by the Association of Official Agricultural Chemists, U.S.A. (1930).

TABLE 4.

Physical and Chemical Constants.

	Local	Spanish
Specific Gravity, 28·5°C ..	0·9090	0·9088
Butyro Refractometer, 40°C..	54·00	55·00
Lovibond Tintometer Yellow .	4·00	3·00
Lovibond Tintometer Red .	0·48	0·56
Acid Value	1·74	2·28
Saponification Value	189·08	191·00
Iodine Value (Winkler) ..	100·75	95·43
Iodine Value (Hanus) ..	96·47	90·50
Acetyl Value	15·67	11·65
Reichert Meissel Value	0·25	0·24
Polenske Value	0·20	0·23
Unsaponifiable Matter ..	0·35	0·46
Saturated Acids, percent, (corrected)	16·63	18·05
Unsaturated Acids, percent, (corrected)	77·48	74·68
Iodine Value of Unsaturated Acids	120·25	105·30

Among the striking differences between the two oils may be mentioned, the higher Acetyl and Iodine values of the Local oil. As may be expected from the higher Iodine Value, the percentage of Unsaturated acids is also higher in the Local oil.

The free fatty acids were prepared from the oil by saponification with alcoholic potash and then neutralizing with sulphuric acid. The acids were of pale yellow colour and on standing, the solid acids settled down in the form of fine granules.

The mixed fatty acids were next resolved into solid and liquid acids by twice precipitating them with lead acetate in 95 percent. alcoholic solution according to lead-salt-alcohol method of Twitchell (*Ind. and Eng. Chem.* 1921. *13.* 806).

The table below gives the characteristics of the total fatty acids and the solid and liquid acids.

TABLE 5

	Local	Spanish
Total Fatty Acids.		
Mean Molecular Weight	292·40	292·85
Iodine Value (Winkler)	99·25	94·72
Solid Fatty Acids.		
Mean Molecular Weight	262·20	300·80
Iodine Value (Winkler)	2·62	0·63
Liquid Fatty Acids.		
Mean Molecular Weight	340·30	340·50
Iodine Value (Winkler)	120·25	105·30

The saturated fatty acids were converted into methyl esters using dry hydrochloric acid as a catalyst and distilled fractionally under reduced pressure. Saponification Value, Mean Molecular Weight and Iodine Value (which gives the measure of the contaminating unsaturated acids) were determined for each fraction and actual percentages of individual acids calculated therefrom.

The liquid acids were brominated in ether according to the method described by Jamieson and Baughman (*J. A. C. S.* 1920. *42.* 238; 1921. *43,* 1372). The ethereal solution did not give any precipitate showing the complete absence of linolenic acid. Linoleic tetrabromide was separated from oleic dibromide by the solubiltiy of the latter in petroleum ether.

Table 6 gives the percentages of saturated and unsaturated acids and table 7 gives the percentages of glycerides in the two oils.

TABLE 6.

	Local per cent.	Spanish per cent.
Palmitic	7·75	8·53
Stearic	4·33	2·14
Arachidic	1·45	3·42
Lignoceric	3·10	3·98
Linoleic	24·80	16·69
Oleic	52·67	57·99

TABLE 7.

Glycerides of	*Local*	*Spanish*	* *Spanish*
Palmitic Acid . ..	8·13	8·92	8·20
Stearic Acid . ..	4·52	2·23	6·20
Arachidic Acid .	1·49	3·52	4·00
Lignoceric Acid . ..	3·19	4·10	3·10
Linoleic Acid	25·79	17·36	24·70
Oleic Acid . ..	55·04	60·60	52·90
Unsaponifiable Matter ..	0·35	0·46	0·20

As has already been pointed out, the main differences between the oils of Spanish and Local varieties are the higher Acetyl and Iodine values of the Local oil. Consequently the percentage of the unsaturated acids is also higher in the Local oil by 8·4 per cent or one and half times that in the Spanish oil, which explains the higher Iodine value of the former. Finally the characteristic fatty acid of Ground-nut Oil—Arachidic Acid—is less in the Local oil than in Spanish oil, while Stearic acid content is double in the Local.

In the same table column 4 gives the results of the analysis of the oil of the Spanish variety, but grown in a different country under different conditions of soil and climate. As can be seen in the table the three oils differ in their composition. The main differences observed are in the contents of Stearic and Arachidic acids. Thus the oils from different varieties and also of the same variety but grown under different conditions show variations in their composition.

The authors are thankful to Rao Bahadur Dr. D. L. Sahasrabuddhe for suggesting this problem and for his help and advice while this investigation was in progress.

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* Jamieson, Baugham and Brans, *J. A. C. S.* 1921, *43*, 1372.

A NOTE ON MAXIMA AND MINIMA

By

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In applying the methods of the Infinitesimal Calculus to the consideration of the turning points of a continuous differentiable function, the following *sufficient* set of conditions are often given :

If in the neighbourhood of $x = a$, $f'(x) > 0$ when $x < a$, and $f'(x) < 0$ when $x > a$, $f(a)$ is a maximum value of $f(x)$; and similarly for a minimum, with appropriate changes. (A)

To shew that these conditions are not necessary consider the following interesting examples :

Let $f(x) = x^2 \left(2 + \sin \frac{1}{x}\right)$ when $x \neq 0$, and $f(0) = 0$.

In a neighbourhood of $x = 0$, $f(x)$ oscillates between x^2 and $3x^2$ and so is positive, except at $x = 0$ where it is 0.

$\therefore f(0) < f(x)$ where $x \neq 0$.

$\therefore f(0)$ is a minimum value.

But $f'(x) = 4x + 2x \sin \frac{1}{x} - \cos \frac{1}{x}$ when $x \neq 0$, and $f'(0) = 0$.

$\therefore f'(x)$ hasn't got a constant sign in the neighbourhood of $x = 0$, and so the conditions (A) cannot be satisfied.

If $f(x) = x^2\left(1 + \sin \frac{1}{x}\right)$ when $x \neq 0$, and $f(0) = 0$, $f(0)$ is still a minimum value, although $f(x) = f(0)$ also at other points in every neighbourhood of $x = 0$. On this account some may even hesitate to regard it as a minimum.

If $f(x) = x^4 \left(2 + \sin \frac{1}{x}\right)$ when $x \neq 0$, and $f(0) = 0$, $f(0)$ is a minimum ; here $f'(x)$ is *continuous* at 0, but still it does not satisfy (A).

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PROPAGATION OF LIGHT WAVES THROUGH ETHER

By

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[The object of this article is to shew that if the light waves are considered as plane waves, their nature can be studied first by guessing the solution and then determining it so as to be in conformity with the physical facts.]

Propagation of light waves takes place through the elastic medium of ether.

Consider a molecule of ether. Let M be the molecule of ether in the state of equilibrium. Due to the vibration let it occupy the position M_1. Then MM_1 would be the vector of displacement of the molecule at M. If (x, y, z) are the coordinates of M and $(x + u, y + v, z + w)$ those of M_1 referred to three rectangular axes then (u, v, w) would be the components of displacement of MM_1. The components of the velocity of the molecule would be

$$\frac{\partial u}{\partial t},\ \frac{\partial v}{\partial t},\ \frac{\partial w}{\partial t}$$

and those of acceleration

$$\frac{\partial^2 u}{\partial t^2},\ \frac{\partial^2 v}{\partial t^2},\ \frac{\partial^2 w}{\partial t^2}$$

Now consider a small parallelepiped having its edges passing through the molecule M and parallel to the coordinate axes. Let the lengths of the conterminous edges be δx, δy, δz. Then its volume ω is given by

$$\omega = \delta x\ \delta y\ \delta z.$$

Due to the vibration, the parallelepiped is displaced from one position to the other. Consider two such consecutive positions. In the second position it is obvious that the edges of the parallelepiped may or may not be parallel to the coordinate axes.

Then the equations of small movements can be obtained by resolving the motion parallel to the x, y, z axes respectively.

Thus resolving parallel to the axis of x we get

$$\frac{\partial^2 u}{\partial t^2}\rho\,\delta x\,\delta y\,\delta z = -N_1\,\delta y\,\delta z + \left(N_1 + \frac{\partial N_1}{\partial x}\partial x\right)\partial y\,\partial z$$

$$-T_3\,\delta z\,\delta x + \left(T_3 + \frac{\partial T_3}{\partial y}\partial y\right)\delta z\,\partial x$$

$$-T_2\,\delta x\,\delta y + \left(T_2 + \frac{\partial T_2}{\partial z}\delta z\right)\delta x\,\delta y$$

where ρ is the density of the parallelepiped, N_1, N_2, N_3 are the normal stresses (normal to the faces of the parallelepiped) and T_1, T_2, T_3 are the tangential stresses acting along the faces of the parallelepiped.

The above equation reduces to

$$\rho\frac{\partial^2 u}{\partial t^2} = \frac{\partial N_1}{\partial x} + \frac{\partial T_3}{\partial y} + \frac{\partial T_2}{\partial z}$$

Similarly resolving parallel to the y and z axes we can easily get

$$\rho\frac{\partial^2 v}{\partial t^2} = \frac{\partial T_3}{\partial x} + \frac{\partial N_2}{\partial y} + \frac{\partial T_1}{\partial x}$$

$$\rho\frac{\partial^2 w}{\partial t^2} = \frac{\partial T_2}{\partial x} + \frac{\partial T_1}{\partial y} + \frac{\partial N_3}{\partial z} \quad \dots\dots\dots\dots \quad (1)$$

But u, v, w, the components of molecular displacement and N_1, N_2, N_3, T_1, T_2, T_3 are connected by the following relations :

$$N_1 = \lambda\Delta + 2\mu\frac{\partial u}{\partial x} \quad \text{and} \quad T_1 = \mu\left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\right)$$

$$N_2 = \lambda\Delta + 2\mu\frac{\partial v}{\partial y} \qquad T_2 = \mu\left(\frac{\partial w}{\partial x} + \frac{\partial u}{\partial z}\right)$$

$$N_3 = \lambda\Delta + 2\mu\frac{\partial w}{\partial z} \qquad T_3 = \mu\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right)$$

Where λ, μ are known constants [μ being the modulus of rigidity and $(\lambda + \frac{2}{3}\mu)$ modulus of elasticity or the modulus of compression] and Δ is the cubical dilatation.

By substituting these values in (1) we get :

$$\left.\begin{aligned}
\rho\frac{\partial^2 u}{\partial t^2} &= (\lambda + \mu)\frac{\partial\Delta}{\partial x} + \mu\nabla^2 u \\
\rho\frac{\partial^2 v}{\partial t^2} &= (\lambda + \mu)\frac{\partial\Delta}{\partial y} + \mu\nabla^2 v \\
\rho\frac{\partial^2 w}{\partial t^2} &= (\lambda + \mu)\frac{\partial\Delta}{\partial z} + \mu\nabla^2 w
\end{aligned}\right\} \quad \dots\dots \quad (2)$$

Theory of plane waves :—If now the light waves be considered as plane waves and if they are propagated in such a manner that they are parallel to the xy plane, then u, v, w, the components of displacement would depend only upon *z* and *t*.

Thus in this case

$$\frac{\partial\Delta}{\partial x} = \frac{\partial\Delta}{\partial y} = 0$$

$$\text{and } \nabla^2 u = \frac{\partial^2 u}{\partial z^2}, \ \nabla^2 v = \frac{\partial^2 v}{\partial z^2}, \ \nabla^2 w = \frac{\partial^2 w}{\partial z^2}$$

$$\text{and } \Delta = \frac{\partial w}{\partial z}.$$

Then the equations (2) further reduce to :

$$\left.\begin{aligned} \rho\frac{\partial^2 u}{\partial t^2} &= \mu\frac{\partial^2 u}{\partial z^2} \\ \rho\frac{\partial^2 v}{\partial t^2} &= \mu\frac{\partial^2 v}{\partial z^2} \\ \rho\frac{\partial^2 w}{\partial t^2} &= (\lambda + 2\mu)\frac{\partial^2 w}{\partial z^2} \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (3)$$

Putting $\omega_1 = \sqrt{\frac{\mu}{\rho}}$ and $\omega_2 = \sqrt{\frac{\lambda + 2\mu}{\rho}}$ we get

$$\left.\begin{aligned} \frac{\partial^2 u}{\partial t^2} &= \omega_1^2\frac{\partial^2 u}{\partial z^2} \\ \frac{\partial^2 v}{\partial t^2} &= \omega_1^2\frac{\partial^2 v}{\partial z^2} \\ \frac{\partial^2 \omega}{\partial t^2} &= \omega_2^2\frac{\partial^2 \omega}{\partial z^2} \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (4)$$

The forms of these equations clearly indicate that they are similar to those of vibrating bodies.

Their general integrals are given by :

$$u = \Phi_1 (z - \omega_1 t) + \Psi_1 (z + \omega_1 t)$$
$$v = \Phi_2 (z - \omega_1 t) + \Psi_2 (z + \omega_1 t)$$
$$w = \Phi_3 (z - \omega_2 t) + \Psi_3 (z + \omega_2 t)$$

the function Φ and Ψ being perfectly arbitrary.

If further, we suppose that

$$v = w = o \text{ and } u \neq o$$

the plane wave being parallel to the xy plane, the vibrations would be transversal and would be propagated with a velocity

$$\omega_1 = \sqrt{\frac{\mu}{\rho}}$$

Similar results would follow if

$$u = w = o \quad v \neq o$$

But if $u = v = o$ and $w \neq o$ then

$$w = \Phi_3 (z - \omega_2 t) + \Psi_3 (z + \omega_2 t)$$

This represents a longitudinal vibration since the displacement is perpendicular to the plane of the wave, the velocity of propagation being

$$\omega_2 = \sqrt{\frac{\lambda + 2\mu}{\rho}}$$

In this case

$$udx + vdy + wdz$$

reduces to wdz

and w being a function of z and t only, wdz is a perfect differential.

The quantities w_1 and w_2 are thus the velocities of the transverse and longitudinal waves and they are in general different from each other.

But here it should be borne in mind that light vibrations are always transversal. Hence in the various phenomena of reflection and refraction, the force of the incident ray is visible in the transverse vibration. Had the vibration been longitudinal, the part of the force would have been absorbed.

Hence it is here essential to take that the longitudinal vibration does not exist for a ray of light.

Hence in order to keep conformity with the physical facts these mathematical equations must satisfy the equation :

$$\omega_2 = o$$

or $$\lambda + 2\mu - o$$

Instead of taking the xy plane (i.e. $z = o$) if the plane

$$\alpha x + \beta y + \gamma z = o$$

be taken parallel to the plane of the wave, then the quantities u, v, w would be functions of $\alpha x + \beta y + \gamma z$ and t.

Let us now consider the particular case corresponding to the periodic vibrations. The equations that give u, v, w are to have real coefficients if we find a solution :

$$u = u_0$$

$$v = v_0$$

$$w = w_0$$

or if, u_0, v_0, w_0 are imaginary, we shall denote u'_0, v'_0, w'_0 their imaginary conjugates and the equations will be satisfied by

$$u = u'_0 \,;\; v = v'_0 \,;\; w = w'_0$$

Hence the new solutions would be given by :

$$u = \tfrac{1}{2}\,(u_o + u'_o)$$

$$v = \tfrac{1}{2}\,(v_o + v'_o)$$

$$w = \tfrac{1}{2}\,(w_o + w'_o)$$

i.e. by the real parts of u_o, v_o, w_o.

We can therefore write u, v, w under the complex form and consider only the real part of this complex function.

For studying periodic vibrations we shall take u, v, w as the complex functions in the exponential form say

$$u = Ae^{i(\alpha x + \beta y + \Upsilon z + pt)}$$

$$v = Be^{i(\alpha x + \beta y + \Upsilon z + pt)}$$

$$w = Ce^{i(\alpha x + \beta y + \Upsilon z + pt)}$$

or writing $P = \alpha x + \beta y + \Upsilon z + pt$

$$u = Ae^{iP}$$

$$v = Be^{iP}$$

$$w = Ce^{iP}$$

The plane of the wave is always

$$\alpha x + \beta y + \gamma z + pt = o$$

being parallel to $\alpha x + \beta y + \gamma z = o$

Let us try to find out the transverse waves.

The conditions that the wave should be transversal is that the deformation should be transverse. For this to be so

$$\Delta = o$$

i.e. $$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = o$$

i.e. $$Ai\alpha e^{iP} + Bi\beta e^{iP} + Ci\Upsilon e^{iP} = o$$

or $$A\alpha + B\beta + C\Upsilon = o$$

Hence the direction of vibration is in the plane of the wave.

Now $$\frac{\partial^2 u}{\partial t^2} = \omega_1^2\,\nabla^2 u$$

i.e. $$\frac{\partial^2 u}{\partial t^2} = \omega_1^2\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right) \quad \ldots\ldots, \quad (5)$$

But $u = Ae^{i(\alpha x + \beta y + \gamma z + pt)} = Ae^{iP}$

$$\therefore \frac{\partial u}{\partial x} = Ai\alpha e^{iP}$$

$$\therefore \frac{\partial^2 u}{\partial x^2} = -A\alpha^2 e^{iP}$$

$\therefore$ the equation (5) gives

$$-p^2Ae^{iP} = -\omega_1^2(\alpha^2 + \beta^2 + \gamma^2)Ae^{iP}$$

or $p^2 = \omega_1^2(\alpha^2 + \beta^2 + \gamma^2)$.

Taking various forms for the periodic vibration, we can thus study the mathematical nature of the propagation of light waves.

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SOLUTION OF THE BERNOULI—EULERIAN THEOREM ON BENDING OF RODS.

By

PROF. L. V. GURJAR, M.A.

(Before reading this article, the reader is requested to go through my article on the solution of the problem of St. Venant that appeared in the *Bombay University Journal*, Vol. V part II, September, 1936, pp. 172-176.)

Statement :—

"The bending moment at any point is proportional to the curvature at the point."

Take a cylinder ABba and let CD be a right section of it. Then the portion ABDC will be in equilibrium under the action of :

(*i*) The external forces applied at the base ;
(*ii*) the mutual internal molecular action ;
(*iii*) the reaction of the part CDba i.e. the pressures upon the various elements of CD.

Take the origin at the centre of gravity of the cylinder and the axes of coordinates the principal axes of inertia at the point, the axis of z being parallel to the generators of the cylinder.

Let o' of the point of CD where the z axis cuts it (o' will obviously be the centre of CD) and draw $o'\,x'$, $o'\,y'$ parallel to ox, oy respectively. Then it follows that $o'\,x'$, $o'\,y'$, $o'\,z$ will be the axes of inertia for CD.

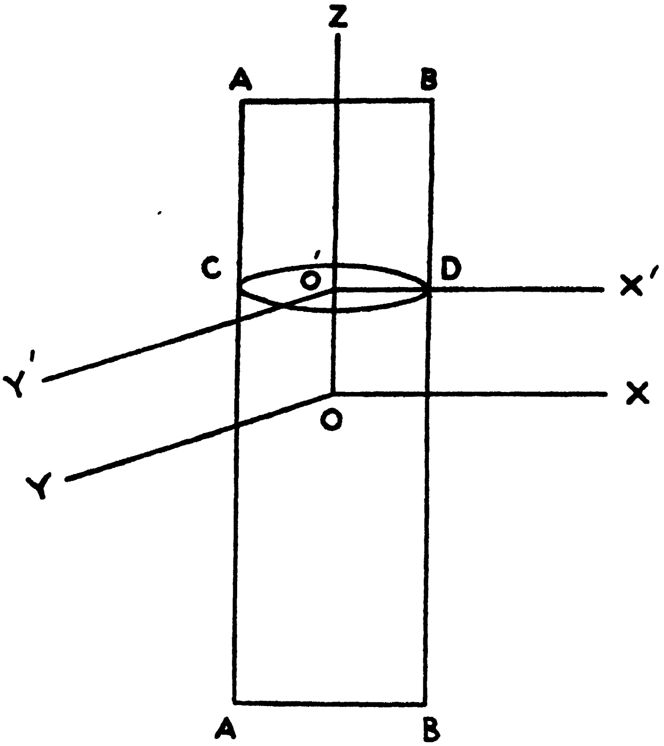
Let $d\omega$ be the element of the area CD. Then pressures upon this element will be (since it is parallel to the xy plane)

$$T_2 d\omega,\ T_1 d\omega,\ N_3 d\omega$$

where N_1, N_2, N_3 are the normal stresses and T_1, T_2, T_3 the tangential ones (See Lame's Lécons del'elasticité).

All these pressures on the elementary areas of CD can be combined so that we get a single resultant pressure whose point of application is at O′ together with a couple called the resultant couple.

The moment of this couple about the axis of $o'x'$ or the axis $o'y'$ is called *the bending moment* and the moment about $o'\,z$ is called the moment of the *torsion couple.*



The components of the resultant pressure upon CD are :

$$\iint T_2 d\omega, \qquad \iint T_1 d\omega, \qquad \iint N_3 d\omega$$

The bending moment about the axis of x is therefore

$$\iint N_3 \, y d\omega$$

and that about the axis of y is

$$-\iint N_3 \, x \, d\omega$$

The moment of *torsion* is :

$$\iint (xT_1 - y\,T_2) \, d\omega$$

If F is the force applied to the base AB, the following is the total action of forces upon ABDC :

(*i*) the force F ;

(*ii*) the mutual internal molecular actions ;

(*iii*) the pressures exerted upon various elements of the area CD.

Of these the mutual molecular actions being equal and opposite neutralise each other.

Consequently F is the only force which in conjunction with the pressures upon the various parts of CD ensures the equilibrium of ABDC. Hence the bending moments of pressures about the axes of o′ x′ and o′ y′ and the moment of torsion couple about o′ z will be equal to the corresponding moments of F about the axes o′ x, o′ y,′ o′ z respectively.

Curvature :—Now take some fibre of the cylinder and let any point on CD whose coordinates are (o, o, z) have coordinates (u, v, z + w) after deformation where w is very small—almost negligible so that we can take the coordinates as (u, v, z).

The projection of the curvature (for, the mean fibre would become curved due to the deformation) upon the vertical plane zx is the curvature at the point (u, z) and is given by

$$\frac{1}{\rho} = \frac{\partial^2 u}{\partial z^2} \Big/ \left[1 + \left(\frac{\partial u}{\partial z}\right)^2\right]^{\frac{3}{2}}$$

Neglecting the square of $\frac{\partial u}{\partial z}$ which is infinitely small we have

$$\frac{1}{\rho} = \frac{\partial^2 u}{\partial z^2} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

This curvature we are now going to shew to be proportional to the bending moment.

According to the Saint Venant's problem, we get

$$u + iv = a + bx + cx^2 = f\,(x,\ z)$$

where b and c are polynomials of the first degree and a is of the third degree in z, and $x = x + iy$

Then

$$\frac{\partial^2 u}{\partial z^2} + i\,\frac{\partial^2 v}{\partial z^2} = \frac{\partial^2 a}{\partial z^2} \quad \text{where } \frac{\partial^2 u}{\partial z^2} \text{ is the real part of } \frac{\partial^2 a}{\partial z^2}$$

It therefore follows that the curvature does not depend upon (x, y) but upon z and so is the same for all the points of the fibres that cut the same right section.

Now let

$$b = b_0 + ib_1$$

$$c = c_0 + ic_1$$

where b_0, c_0 are real parts of b and c and b_1, c_1 the imaginary.

It also follows from the solution of the Saint Venant's problem that

$$\frac{\partial^2 a}{\partial z^2} = \frac{2}{\sigma} c$$

where $\sigma \quad \frac{\lambda}{2(\lambda + \mu)}$

$$\therefore \quad \frac{\partial^2 a}{\partial z^2} = 4\frac{\lambda + \mu}{\lambda} c$$

But $\frac{\partial^2 u}{\partial z^2}$ is the real part of $\frac{\partial^2 a}{\partial z^2}$ and c_o that of c. It follows that

$$\frac{\partial^2 u}{\partial z^2} = 4\frac{\lambda + \mu}{\lambda} C_o$$

To calculate the bending moment we have :

$$N_3 = \lambda \Delta + 2\mu \frac{\partial w}{\partial z}$$

$$N_1 = \lambda \Delta + 2\mu \frac{\partial u}{\partial x} = o$$

$$N_2 = \lambda \Delta + 2\mu \frac{\partial v}{\partial y} = o$$

Adding these

$$N_3 = 3\lambda \Delta + 2\mu \Delta = (3\lambda + 2\mu)\Delta$$

$$= -\frac{2\mu}{\lambda}(3\lambda + 2\mu)\frac{\partial u}{\partial x}$$

Since $\Delta = -\frac{2\mu}{\lambda}\frac{\partial u}{\partial x}$.

Again $u + iv = a + bx + cx^2 = f(x, z)$

$$\therefore \quad \frac{\partial u}{\partial x} + i\frac{\partial v}{\partial x} = \frac{\partial f}{\partial x} = b + 2cx$$

$\therefore \quad \frac{\partial u}{\partial x}$ is the real part of $b + 2cx$

$$\therefore \quad \frac{\partial u}{\partial x} = b_o + 2c_o x - 2c_1 y$$

$$\therefore \quad N_3 = -\frac{2\mu}{\lambda}(3\lambda + 2\mu)(b_o + 2c_o x - 2c_1 y)$$

$\therefore$ the bending moment is given by

$$-\int\int N_3 x\,d\omega = \frac{2\mu}{\lambda}(3\lambda + 2\mu)\left\{ b_o \int\int x\,d\omega + 2c_o \int\int x^2 d\omega - 2c_1 \int\int xy\,d\omega \right\}$$

But $\iint x d\omega = o$ since o′ is the centre of the section CD,

and $\iint xy d\omega = o$ since o′ z is the axis of inertia.

$$\therefore \quad -\iint N_3 x d\omega = \frac{2\mu}{\lambda}(3\lambda + 2\mu)\, 2c_0 \iint x^2 d\omega$$

Since $\iint x^2 d\omega = I$, the moment of inertia of the right section about o′y′ and

$$c_0 = \frac{\lambda}{4(\lambda + \mu)} \frac{\partial^2 u}{\partial z^2}$$

$$\therefore \quad -\iint N_3 x d\omega = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}\, I \,\frac{\partial^2 u}{\partial z^2} = \frac{EI}{\rho}$$

since $\quad \dfrac{1}{\rho} = \dfrac{\partial^2 u}{\partial z^2}$

and $\quad \dfrac{\mu(3\lambda + 2\mu)}{\lambda + \mu} = E \quad$ (the Young's modulus).

The bending moment is therefore proportional to the curvature.

Hence in all problems of bending of rods we take the bending moment proportional to the curvature and equate to it the corresponding moments of the force F applied at the end AB.

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THEORY OF MAGNETISM—(A SUMMARY)

By

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INTRODUCTION

In general when we bring a substance in a magnetic field of strength H_a, it shows magnetic polarisation. If F is the amount of magnetic moment induced per unit volume, then the field when the substance is present is different from the field H_a in vacuum.

$$H = H_a + H_i = H_a + \text{grad}\left(\int\int \frac{F_n\, df}{r} - \int\int\int \frac{\text{div } F}{r} dv\right)$$

where F_n is the component of F normal to the surface element df; and dv is the element of volume inside this surface. The value of F depends on the nature of the substance, is independent of the shape of the body and is a function of the field strength H.F.$=F(H)$. If we divide F into two components one parallel to H and the other perpendicular to H, for most * substances F_n vanishes and we write $F_{||} = F\ (H)$. Most important is the rate of change of $F_{||}$ in weak magnetic fields. The quantity $\chi = \left(\frac{\partial F_{||}}{\partial H}\right)_{H \to O}$ is the magnetic susceptibility. Sometimes we consider the susceptibility pro Mol $\chi_L = v\chi$, where v = Mol volume.

(a) *Diamagnetic substances.* Here χ is negative and in general so small that at normal temperatures and with practically attainable fields, there is a linear relation $F_{||} = \chi H$. In general the diamagnetic susceptibility pro Mol is independent of the temperature. The rare gases are diamagnetic, *e.g.*, for helium $\chi_L = -18{\cdot}8 \times 10^{-7}$.

(b) *Paramagnetic substances.* Here χ is positive and varies with temperature.

1. In the case of O_2 gas $\chi = \frac{C}{T}$ where C is a constant and T the absolute temperature. At room temperature and atmospheric pressure $\chi = 1{\cdot}4 \times 10^{-7}$.

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* Isotropic bodies, and anisotropic bodies when H is along one of the principal magnetic axes.

2. For solid Na, upto melting point χ is independent of temperature and is $5{\cdot}8 \times 10^{-7}$.

3. Solid iron above 1100° K follows the law of Curie and Weiss $\chi = \dfrac{C}{T\Theta_p}$ where Θ_p is the paramagnetic curie point and is about 1050° K.

(c). *Ferromagnetism.* Pure single crystals of ferromagnetic substances show even in weak fields a finite magnetisation. Here χ is positive and very large as compared with other substances; it varies between 50 and 30,000 depending on the previous history and the state of tension. $F_{||}$ is not here a definite function of H, and although hysterisis is a characteristic of ferromagnetism its magnitude is a result of the tension and the impurities and is practically negligible in pure single crystals. Ferromagnetic substances are Iron, Nickel and Cobalt, under the temperatures 1040°, 631°, 1404° K respectively. The temperature above which a substance ceases to be ferromagnetic, is called its ferromagnetic Curie point and is denoted by Θ_f.

As χ is in general small we may write $H = H_a$. However in the case of ferromagnetic substances the limiting field H_l plays an important part. The problem before the molecular theory of magnetism is to explain the magnetic properties of matter in terms of the accepted structure of the atoms, namely the nucleus electron model.

(*Note* : Only the significance of the special symbols is given.)

DIAMAGNETISM OF ATOMS AND MOLECULES

Consider a monatomic gas in which the electrons are influenced by the coulomb field of the nucleus (we neglect the relativity spin of the electron). In the presence of a magnetic field H, in the Z direction, there is superimposed on the normal electron motion a rotation, the Larmor precession $\omega = -\dfrac{eH}{2\,m_0\,c}$ while the moment of rotation induced by this external field is given by

$$m = -m_0\,\omega \sum_i (x_i^{\,2} + y_i^{\,2}).$$

Thus the magnetic moment. is $M = -\dfrac{em}{2\,m_0c} = -\dfrac{e^2H}{4\,m_0c^2}\sum_i (x_i^{\,2} + y_i^{\,2})$

Actually we observe not this instantaneous value but the time average of M. $\overline{M} = -\dfrac{e^2H}{4m_0c^2}\sum_i (\overline{x_i^{\,2} + y_i^{\,2}})$

In the absence of the external field, all directions are of course equally probable, and we get $\overline{x_i^2} = \overline{y_i^2} = \overline{z_i^2} = \left(\frac{\overline{r_i^2}}{3}\right)$

where r_i is the distance of the ith electron from the nucleus. Thus

$$\overline{M} = -\frac{e^2H}{6m_0c^2}\sum_i \overline{r_i^2}$$

If N is the number of atoms per unit volume and we assume that the moment induced by the external field, is the only magnetic moment the atom possesses, we get

$$J = N\overline{M} = -N\frac{e^2H}{6m_0c^2}\sum_i \overline{r_1^2} \text{ and } \chi = -\frac{Ne^2}{6m_0c^2}\sum \overline{r_i^2}$$

If we substitute for $r_1 \approx 1{\cdot}0 \times 10^{-8}$ cm. we obtain the values of χ which are of the same order as those actually observed.

In the quantum theory we again consider a system of n electrons influenced by the external field H and the electrostatic field of the nucleus. We get for the average $\overline{M}$ (neglecting H^2 etc.) in the ground state of the atom or molecule

$$\overline{M} = \overline{M}_0 - \frac{He^2}{4m_0c^2}\sum_i(\overline{x_i^2} + \overline{y_i^2}) + 2H\sum_{s \neq 0}\frac{|M_{s0}|^2}{E_s - E_0}$$

M is the average moment in the ground state which would be zero if we assume that the ground state is not degenerate. For an atom or ion when the nuclear field is spherically symmetrical the third term vanishes. This can be seen very easily, for if we neglect the spin, the magnetic moment $M = -\frac{e}{2m_0c}$ m, where m is the Drehimpuls moment, but now the time average of m is constant, thus in every stationary state the matrix element M_{s0} vanishes.

Thus in the case of a spherically symmetrical nuclear field we receive $\overline{M} = -\frac{e^2H}{4m_0c^2}\sum_i(\overline{x_i^2} + \overline{y_i^2})$

the same as classical. In the case of molecules with more atoms the field is not symmetrical and the third term does not vanish. Still χ will be of the same order of magnitude as for the atoms.

DIAMAGNETISM OF METALS

Various properties of the metals, specially the conductivity, were explained by Drude and Lorentz, taking the electrons as free (about one per atom) and assuming they behave as a gas and obey the Boltzmann statistics. But the concentration of the electron gas at the normal temperatures is so large, that it is necessary to use the

Fermi statistics. Landau was able to show that these conductivity electrons, following quantum laws show a diamagnetism.

The free energy of a Fermi gas of N electrons is given by

$$F = N\omega + \Omega \text{ where } \Omega = -kT \sum_s \log \left[1 + \varepsilon^{(\omega - E_s)/kT}\right]$$

and ω is the chemical potential and is determined from N by the relation $N = -\frac{\partial \Omega}{\partial \omega} = \sum_s \frac{1}{\varepsilon^{E_s - \omega/kT} + 1}$

the summation extends over all the stationary states of the electron.

We get for the average magnetic moment

$$\overline{M} = -\frac{\partial F}{\partial H} = \left(N\frac{\partial \omega}{\partial H} + \frac{\partial \Omega}{\partial \omega}\frac{\partial \omega}{\partial H} - \frac{\partial \Omega}{\partial H}\right) = -\frac{\partial \Omega}{\partial H}$$

The problem here is to determine the various E_s—the stationary states of energy E_s for an electron inside a metal under the influence of a magnetic field H. If we write $\overline{M} = M_1 + M_2$ where M_1 is the contribution of the electrons inside the metal and M_2 is the contribution of the electrons at the boundary or near the walls, we get

$$\Omega = \Omega_0 - \frac{H^2 \mu_0^2}{6} \frac{\partial^2 \Omega_0}{\partial \omega^2}$$

Here Ω_0 is the value of Ω in the absence of the external magnetic field and $\mu_0 = \frac{eh}{4\pi m_0 C} = 0{\cdot}91 \times 10^{-20}$ c.g.s. unit—the Bohrmagneton.

(As paramagnetism in weak fields due to the electron spin gives $\Omega = \Omega_0 + \frac{H^2 \mu_0^2}{2} \frac{\partial^2 \Omega_0}{\partial \omega^2}$, we see that the diamagnetic susceptibility is $^1/_3$ the paramagnetic susceptibility due to the spin).

If we go to the Boltzmann statistics we get

$M = -N\mu_0 \left\{\coth \frac{H\mu_0}{kT} - \frac{kT}{H\mu_0}\right\}$. If also $n = \left(\frac{N}{v}\right)$ is the number of electrons per unit volume, then $\chi = -\frac{n\mu_0^2}{3kT}$ which follows a Curie law for the temperature dependence, as opposed to the ordinary gases where χ is independent of the temperatures.

In short, the unbreakable link between angular momentum and magnetic moment makes a magnetic atom precess about the direction of the field. This motion of precession is an extra motion of the electrons of the atom, a circulatory motion around the axis supplied by the direction of the field. This extra motion entails an extra current, an extra current is equivalent to an extra magnetic moment, which is the source of diamagnetism or which is diamagnetism. Diamagnetism is precession. This extra motion is produced in all atoms, thus those atoms which do not possess any magnetic moment also show diamagnetism.

LANGEVIN'S THEORY OF PARAMAGNETISM OF CASES

He assumes that every atom or molecule possesses a spontaneous moment μ, and that in the absence of the external field, as there is no preferential orientation, the resulting moment is zero. Whereas the field orientates the molecules and gives a resulting moment. Let θ be the angle the moment makes with the field and ϕ the azimuth. The energy in the field $E = -H \mu \cos \theta$. The probability for the occurrence of this energy is $\varepsilon^{\mu H \cos \theta / kT}$, but if all the orientations for an atom are equally possible, we must multiply by the element of the solid angle in the neighbourhood of θ and ϕ i.e. $d \Omega = \sin \theta \, d\theta d \phi$

The number of states Z for a gas of N molecules is

$$Z = \left(\int_0^{2\pi} d \phi \int_0^{\pi} \varepsilon^{\mu H \cos \theta / kT} \sin \theta \, d \theta \right)^N$$

The free * energy $F = -N k T \log\left(\frac{4 \pi k T}{\mu H} \sinh \frac{\mu H}{kT}\right)$

The average magnetic moment $\overline{M} - -\frac{\partial F}{\partial H} = N \mu \left(\coth \frac{H \mu}{k T} - \frac{k T}{\mu H} \right)$

and the susceptibility $\chi = n \mu^2 / 3 k T$.

From the experimentally known values of χ we can calculate μ which comes out approximately $\mu \sim 1 \times 10^{-20}$ c.g.s. unit as compared with the Bohr magneton $\mu_0 = \frac{eh}{4 \pi m_0 c} = 0{\cdot}91 \times 10^{-20}$ c. g. s. unit.

In the Quantum theory of diamagnetism we neglected the relativity spin of the electron, but we have to take this into account for paramagnetism.

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*The sum of the states $Z = \sum_s \varepsilon^{-E_s/kT}$ is coupled with the free energy of the system F, at the absolute temperature T by the relation $F = -kT \log Z$ where K is the Boltzmann constant.

To obtain the value of χ for *atoms and molecules* we must obtain an expression for the average moment of a system of electrons in the field of force of the nucleus and the external magnetic field H. In obtaining this expression we have to consider the relation between the spin and the orbital moments of the electron the so called coupling. With the normal or Russel-Saunders coupling, which we use in this connection, the spin impulse of the electrons can be given by the vector $\frac{h}{2\pi}$ S, the orbital impulse is given by $\frac{h}{2\pi}$ K, and the two together give the vector $\frac{h}{2\pi} J = \frac{h}{2\pi} (S + K)$.
While the states with different values of $|S| = s$ and $|K| = k$ are energetically widely separated from one another, the states with different $|J| = j$ that is with different inclinations of S and K are comparatively much less separated terms of a multiplet.

At the absolute zero of temperature we can calculate the para magnetism in a quite *elementary way* and we are justified in doing this as the magnitude of paramagnetism is practically independent of the temperature.

When a magnetic field acts on electrons in the metals, they try to arrange themselves so that the spins are parallel to the field, for then the energy is 2H μ_0 times less as when the spins are antiparallel, where μ_0 is the Bohr magneton. If through the spin arrangement the metal has a magnetic moment in the direction of the field, it is paramagnetic and the energetically lowest states are always occupied. In the absence of the magnetic field, the energy of the electron is its energy of motion in the potential field of the metal. Every one of the states of energy less than ζ_0 is occupied by two electrons with opposite spins. With a magnetic field H the energy of an electron with parallel spin is diminished by H μ_0, while that of one with anti-parallel spin is increased by H μ_0. Here also the electrons occupy all states of energy less than a definite energy ζ, but now (the total energy = orbital energy + magnetic energy). Thus the electrons with field parallel spin occupy states of energy less than $\zeta - \mu_0$ H, while the anti-parallel spin electrons occupy $\zeta + \mu_0$ H states. The states with an energy smaller than $\zeta - \mu_0$ H are doubly occupied, while the states between $\zeta - \mu_0$ H and $\zeta + \mu_0$ H are singly occupied. If N is the number of states per unit energy interval, the number of singly occupied states would be N (ζ) 2H μ_0. The electron in a singly occupied state possesses a moment μ_0 in the direction of the field, whereas the moments cancel in the doubly occupied states. This gives the total magnetic moment of the metal as $M = 2H\mu_0^2 N(\zeta)$ i.e. the susceptibility $\chi = \frac{M}{HV} = 2\,\mu_0{}^2\,\frac{N(\zeta)}{V}$

$$= 1{\cdot}88 \times 10^{-6} \left(\frac{\rho n_0}{A}\right)^{1/3}$$

where ρ is the density, n_0 is the number of free electrons per atom and A is the atomic weight.

The formula, of course, is only an approximate one.

FERRO-MAGNETISM

The first problem of the theory of ferromagnetism is to consider the nature of the elementary magnet. It was natural to assume that the ferromagnetism is due to the motion of the electron in the atom. If the magnetisation is due to this motion, a magnetised body must possess internal moment of momentum, the amount of which about any axis is proportional to the component of the magnetic moment about that axis. Now a magnetic substance on demagnetisation would simultaneously experience a change of moment. If $\Delta\bar{M}$ is the variation of magnetisation and $\Delta\bar{m}$ is the change of the moment of inertia, then $\left|\frac{\Delta\bar{M}}{\Delta\bar{m}}\right| = \frac{e}{2\,m_0\,c}$. This was first specifically pointed out by Richardson in 1908, it was also experimentally verified by Einstein and deHaas. But the later more accurate experiments showed that the result observed was only $\left|\frac{\Delta\bar{M}}{\Delta\bar{m}}\right| = \frac{e}{m_0c}$.

This result could not be explained classically, but is now explained by Heisenberg assuming that it is the orientation of the electron spin that is responsible for the ferromagnetism. Before proceeding further let us consider a fruitful hypothesis due to Weiss (1907). *Weiss* assumed that the effective magnetic field consists of two parts, the applied field H plus an inner field, which is proportional to the magnetic polarisation J per unit volume. Thus the effective field $H' = H + aJ$ where a is a numerical constant. Moreover he assumed, as did Langevin in his theory of paramagnetism, the existence of a spontaneous magnetic moment i.e.

$$J = n\,\mu \left\{ \coth\frac{H\mu}{kT} - \frac{kT}{H\mu} \right\}$$

same as Langevin. But as it has been lately proved that it is the electron spin that is responsible for ferromagnetism, we may use instead of Langevin's J, $J = n\mu_0 \operatorname{tagh}\frac{H\mu_0}{kT}$ which gives the paramagnetic moment of a not degenerate electron gas due to spin. (Here although we do not deviate very much from the original hypothesis of Weiss—he had made no assumptions as to the nature of the inner field—we have an advantage, namely that here we are dealing with an equation that is consistent with Nernst's theory). Thus we assume

after Weiss $J = n\,\mu_0\,\text{tagh}\,\frac{H'\mu_0}{k\,T}$ (1a)

$H' = H + a\,J$ (1b)

Let us consider this equation graphically by introducing dimensionless quantities $y = \frac{J}{n\,\mu_0}$, $x = \frac{H'\mu_0}{k\,T}$, $x_0 = \frac{H\,\mu}{kT}$

This gives $y = \text{tagh}\,x$ (2a) for (Ia)

$y = \frac{k\,T}{n\,\mu_0^2\,a}\,(x - x_0)$, (2b) for (1b)

The intersections of these curves give the values of y for a definite x_0, that is the magnetisation J in an applied field H. For reasonably low temperatures even when H is vanishingly small, a definite polarisation $J = J_0$ is always available. When $H = 0$, $x_0 = 0$ and the straight line (2b) goes through the origin. Now if the slope of (2b) is greater than the slope of the tangent to (2a) at $x = 0$ (i.e. I) the curves do not intersect and no ferromagnetism is available. This does not happen when $\frac{k\,T}{n\,\mu^2_0\,a} < 1$ or $T < \frac{n\,\mu^2_0\,a}{k} = \Theta$.

This is the explanation of Weiss for ferromagnetism as well as the Curie point.

Now for iron the Curie point $\Theta = 1040°$ K. True saturation gives the molecular field $H_M \sim 10^7$ gauss. When $T < \Theta$ for a given value of H, i.e., x_0, the two curves intersect one another at three points or three values of J are admissible. It may be supposed that this corresponds to the hysterisis effect, but the hysterisis effect is only observed for polycrystalline impure substances, and to observe this, fields of a few hundreds of gauss are quite sufficient, while the molecular field H_M is $H_M \sim 10^7$ gauss. We must assume that it is the greatest value of J in the same direction as the field which is stable and physically realised, while the other values are unstable and could not be observed. If the field changes its direcetion, *i.e.*, x_0 changes its sign, the other values of J are stable. The experiments with single crystals show that the time lag of J is extraordinarily small and could not upto now be determined.

To consider the variation of J_0 with temperature, we put $x_0 = 0$ and vary the slope of (2b). Small values of T or low temperatures give small values of the slope, and correspondingly large values of

J_0, $J_0 = n\,\mu_0$ is the largest value of J possible corresponding to the true magnetisation in which all the elementary magnets are parallel,

In the neighbourhood of $T = 0$, $J_0 \approx n\,\mu_0\,(1-2\varepsilon^{-2\,\Theta/T})$

with increasing temperature J_0 increases monotonically and reaches for $T = \Theta$ the value zero as demanded by experiments. In the neighbourhood of the Curie point $J_0 \approx n\mu_0 \sqrt{3\left(1-\frac{T}{\Theta}\right)}$

above the Curie point $J_0 = 0$ and satisfies the paramagnetic relation $J = \chi H$ where $\chi = \frac{n\,\mu_0^2}{k\,(T-\Theta)}$ according to the law of Curie and Weiss.

So qualitatively the theory of Weiss, as improved with the substitution of the spin contribution, is a success, but still there are some difficulties.

ELECTRONAUSTAUSCH (EXCHANGE)

To consider the ferromagnetism of metals we assume, after the molecular model of Heitler and London, that the nuclei are at rest at the lattice points, and the electrons in the completed shells need to be considered only so far as they screen the nuclear field. Thus we have to consider only the valence electrons. We further assume that every atom in the ground state has one electron, this is in the S state, with spherical eigenfunctions, and the orbital impulse zero. We are justified in assuming this as the experiment of Einstein and de-Hass shows that it does not play an important part. Moreover we consider only the electrical forces and neglect the comparatively smaller magnetic forces. In the Weiss theory we considered the magnetic forces only.

Let us consider the eigenfunction of a single unperturbed atom, its middle point given by a vector f with components f_1 f_2 f_3. If any point of the lattice is taken as the origin and a b c are primary translations, its position is given by $r_f = af_1 + bf_2 + cf_3$. As we have neglected the magnetic interaction, we can write its eigenfunction Ψ_f as the product of $\phi_f\ (x\ y\ z)$ a function of the coordinates alone and $U_f(\zeta)$ a function of the spin ζ, which will be zero or one. Thus we get for the eigenfunctions which belong to the same eigen value

$\psi_{f\alpha} = \phi_f\, U_{f\alpha}$ and $\psi_{f\beta} = \phi_f\, U_{f\beta}$.

Thus if there are N atoms in the lattice the system would be 2^N times degene[illegible] , Heisenberg obtained the same value for J, as Weiss given abov[illegible]ing that all the energy values of a term system S are the same as the average energy, this assumption is virtually the same as that of a molecular field and is strictly correct for $T >> \Theta$, the exact solution being not possible. We get for the constant of the

molecular field $a = \frac{I\,Z}{8\,n\,\mu_0^2}$

I is the austausch (exchange) integral and gives the probability of the electron exchange for two atoms say f and f′

$$I_{ff'} = \frac{1}{Z} \int \phi_f\,(1)\,\phi_{f'}\,(2)\,\phi_f\,(2)\,\phi_{f'}\,(1) \left(\frac{Ze^2}{r_{12}} + V_f\,(1) + V_f\,(2) + V_{f'}\,(1) ++ V_{f'}\,(2) \right) d\tau_1\, d\tau_2$$

r_{12} is the distance between the electrons 1 and 2. V_f and $V_{f'}$ are the screened atomic fields ; only for the neighbouring atoms, this plays an important roll, and otherwise $I = O$. *n*, the number of atoms per unit volume. Z is the number of neighbours.

$I = \frac{8k\,\Theta}{Z}$ which should be positive for ferromagnetic substances (crystals) for which Θ the Curie temperature is positive. For iron $I \sim 1{\cdot}4 \times 10^{-13}$ ergs $\sim 0{\cdot}1$ e. volts. Whereas I is negative for H_2 molecules. This leads us to believe that the ferromagnetism should be ascribed to the quantum mechanical exchange forces.

Concluding we may remark that when a magnetic field acts on electrons, they try to arrange themselves so that the spins are parallel to the field for then the energy is less as when the spins are antiparallel. The spins in atoms forming molecules or a crystal can be parallel only when the austauschintegral is positive. In the case of ferromagnetism we are concerned only with the spins of the electrons in the uncompleted shells. The electrons in the completed shells, although they can change place with other atoms, cannont contribute as their spins are already saturated and cannot change the direction.

The conditions for I positive are :

1. The existence of an uncompleted shell with a large azimuthal quantum number.
2. The radius of this shell is small as compared with the lattice spacing. The absolute value of I is proportional to the Curie temperature.

Negative I corresponds to small total spin as these states are numerous they are certainly realised, the magnetic moment is small and we get Dia- or paramagnetism.

Our picture of the ferromagnetic single crystal is like this : We assume that there exist in the crystal elongated elementary portions each with a definite spin direction. The size of these portions depends on the temperature, it cannot be accurately estimated but may be about 200 atoms. These portions are of course different from polycrystals observed in normal metals. In an external magnetic field, those portions whose spin direction is the same as the external field increase their size at the expense of others. The energy required for this is very small and already by fairly small fields are almost all the portions parallel to the magnetic axis of the crystal. If this axis does not coincide with the direction of the external field, increasing the field tends to rotate it till both are in the same direction. And lastly any further increase in the field make the electron spins, parallel (this is the true magnetisation.) At ordinary temperatures this can happen for extremely large fields. It is only in the neighbourhood of the Curie point that the true magnetisation plays an important part.

Magnetic moments of the individual atoms of the ferromagnetic metals are by no means out of the common. Thus it may be seen that iron and its congeners are readily magnetisable, not because their atoms are extraordinarily magnetic—which is not at all the case—but because their atoms possess the curious propensity of cohering together in large groups, developed to an extraordinary degree.

Our physical picture of magnetism is as follows :—

The agents of orientation render a body paramagnetic or ferromagnetic, whereas the precession renders it diamagnetic, and as a result a body can be paramagnetic and diamagnetic or ferromagnetic and diamagnetic at one and the same time.

[*Received 17th June, 1937.*]

THE CHEMICAL CONSTITUTION OF THE SEX HORMONES—A SURVEY OF RECENT WORK

By

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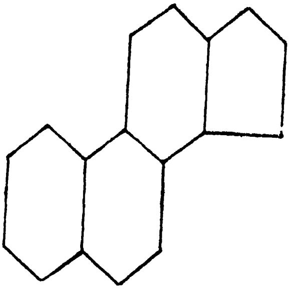
The recent work on the determination of the chemical constitution of the hormones of the sex glands has been the result of the close co-operation of the three allied sciences of biology, chemistry and physiology. The sex-hormones present in the organisms of the vertebrates including man, have the function of bringing about the development of the particular sex, which has been fixed by the number of chromosomes in the cells. Thus it is these substances secreted by the sex glands of the animals, which not only enable the animal to perform its proper functions in the preservation of its race, but also cause the development of the so-called secondary sex-characteristics.

Investigators like Butenandt, Ruzicka, Westphal and others have now established, that there are only three types of sex hormones with substantially different action, which are secreted by the sex-glands of the vertebrates—two by females and one males. Out of the former, one called the *follicle hormone,* is secreted by the ovaries and the other, called the *hormone of the corpus luteum* is secreted by the corpus luteum (yellow body). The male hormone is secreted by the testicles. Butenandt has suggested the name *bio-catalysers* to these hormonic secretions.

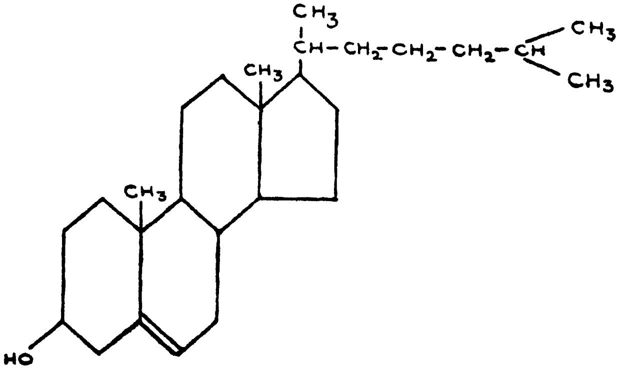
It was only during the last 10 years or so, that the individual hormones have been more exactly defined in their action and this property utilised in examining the purity or otherwise of the chemically fractionated samples.

All the three above mentioned hormones have been isolated from the starting material obtained from the respective glands in the bodies of animals and their chemical constitution determined with a fair amount of certainty. The follicle hormone, Oestrone, which has an empirical formula $C_{18}H_{22}O_2$ was isolated by Doisy and Butenandt from the urine of pregnant women in 1929. The male hormone, Androsterone, with an empirical formula $C_{19}H_{30}O_2$, was isolated from urine of men by Butenandt and Tscherning in 1931. F[illegible] the hormone of corpus luteum, $C_{21}H_{80}O_2$, later called Progesterone, was obtained in the pure condition by Butenandt and Westphal, by Slotta and Fels and by Allen and Wintersteiner practically simultaneously in 1934 using the ovaries of pigs as starting material. As the concentration of these hormones in the starting material is very small the isolation of say 0·1 gm. of these substances meant the use of between 30,000 to 100,000 grams of the raw material. Out of these three hormones, progesterone is present in comparatively larger quantities, although the starting material is more difficult to procure in sufficiently large amounts, and further, the isolated material is more sensitive and unstable. The isolation of these initially unknown substances, could only be achieved by continued physiological experimentation (animal experiments,) just as the accumulation of a radioactive element in a particular sample of material is tested after each operation by electroscopic and other tests.

The first thing that struck the investigators in this field was the similarity in the chemical constitution of these three substances, a fact which was already indicated by the similarity of the empirical formulæ. The cyclo-pentane-perhydro-phenanthrene system shown below appears to be the parent skeleton from which all these sex-hormones are derived :



The fundamentally different actions ot these hormones appear to be due to minor changes in the side-chains and double linkages in the above fundamental four-ring system. The sterines and sterols, substances long known to contain this particular four-ring system are thus closely related to the three sex-hormones. The formula below shows the structure of cholesterine for purposes of comparison.



The sterines are a primary constituent of almost all animal and vegetable cells and are in the position of parent substances of many physiologically important compounds. The best known sterine is the one shown above, the structure of which has now been elucidated by the investigations of Windaus, Wieland, Diels, Rosenheim and others. It may also be mentioned in passing, that vitamin D (irradiated ergosterol) is another compound having the same ring system and is thus closely related to the sex-hormones.

The follicle hormone was the first to be thoroughly investigated. It is secreted by the ovaries of the female and gets continually mixed with the blood-stream. It is this hormone, which, in the human female, causes the sex organs, specially the vagina and the uterus, to develop and also brings about the development of the secondary sex characters, *e. g.*, breasts, female body form, etc. It appears to be the function of this hormone to prepare the uterus for the eventual reception of the fertilised ovum, to fit the body for the actual process of the birth of the child and for its feeding.

The substance Oestrone, $C_{18}H_{22}O_2$, which was first prepared in the pure condition in 1929, when used in animal experiments, is able to produce all the reactions in the female, which the extract of the ovaries containing the original hormone can produce. It can thus be called, with some justification, the pure crystalline form of the follicle hormone. Shortly after the isolation of oestrone, Marrian[1] prepared, in 1930, from the urine of pregnant women, a substance, oestriol, which was chemically different from oestrone, but was qualitatively identical with it in its physiological action on the female animal. The work of Girard and Doisy has shown, that besides these two, there are other substances which can also bring about the same physiological actions, although they are chemically quite different compounds. It is thus clear, that the follicle hormone can be represented by a group of substances, which, on the basis of their physiological action, could all be designated as the pure crystalline forms of the hormone of the follicle. Of course the quantities of these compounds necessary to bring about the same physiological action are different. All these compounds are grouped together under the name of the oestrone group. Table I gives the names etc., of the five most important compounds of this group. (The activity of these compounds is generally measured in some arbitrary units, generally the quantity, dissolved in a fixed quantity of a solvent, sufficient to produce a certain definite reaction in an animal, usually a mouse or a guinea pig. In the case of the oestrone group, the unit used is the mouse-unit, being that quantity, which, when injected in the form of a solution in 0·1 ccm. of sesame oil into a castrated mouse, brings about the appearance of full rut.)

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[1] Lancet, *1935*, 674.

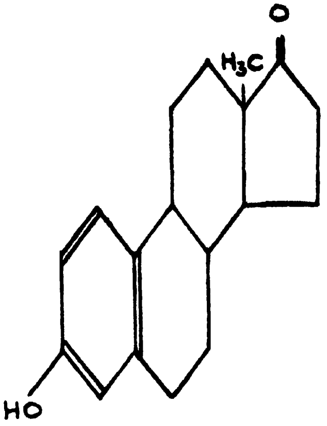
TABLE I.

Name	Formula	Isolated from	Relative activity
Oestrone	$C_{18}H_{22}O_2$	Ovaries Palm kernel Mares' urine	0·1
Oestradiol	$C_{18}H_{24}O_2$	Ovaries Mares' urine	0·05
Oestriol	$C_{18}H_{24}O_3$	Placenta Pregnant women's urine	10
Equiline	$C_{18}H_{20}O_2$	Mares' urine	0·8 (?)
Equilenine	$C_{18}H_{18}O_2$	do do	2 (?)

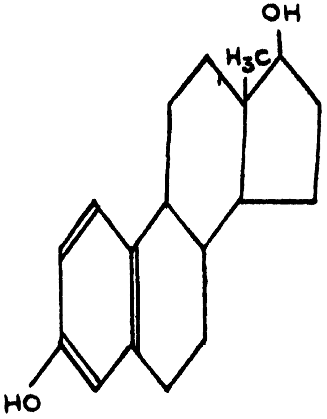
N. B. The numbers in column 4 show that oetsradiol, of which the smallest quantity is necessary to produce the rut in the castrated rat, is the most powerful compound in this group

Our ideas about the specific action of hormones have necessarily been considerably modified by the above discoveries and it may be said, that the action of all these compounds is due to their general chemical nature and that minor changes in the substituents or the positions of double linkages only affect the activity. The question whether the body manufactures all these compounds as primary products of the glands or whether only the most reactive compound is manufactured by the body and the others are then produced by its transformation and modification, can only be answered by further work.

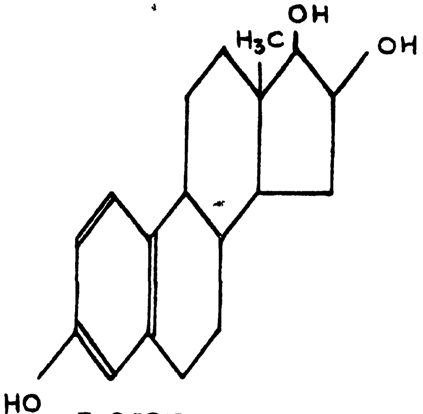
The chemical constitutions of the above five substances are given below :



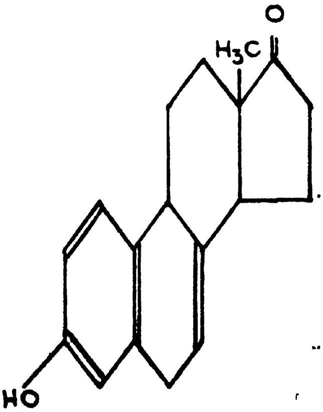
1. OESTRONE



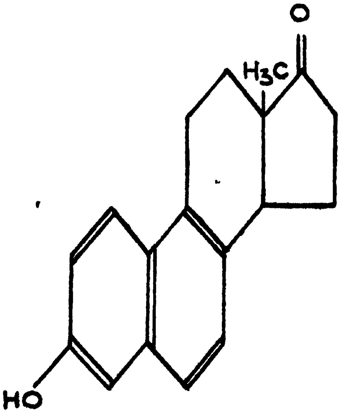
2. OESTRADIOL



3. OESTRIOL



4. EQUILINE



5. EQUILENINE

It will be seen that the four-ring system is common to all these substances. I shall not go into the details regarding the analytical and synthetical methods used in the determination of the constitutions of these substances. Suffice it to say, that oestriol can be transformed into 1-2-dimethyl-phenanthrene by fusion with alkali and subsequent action of selenium and distillation with zinc dust. Cook[1] has further shown, that oestrone can be decomposed to 7-methoxy-1-2-cyclopentenophenanthrene, which has been synthesized in the laboratory.

The testicle hormone can be regarded as the antipode of the follicle hormone, as it causes the specifically male characteristics to develop, *e.g.* the horns of a stag, the comb of a cock or the moustaches of a man. The activity of the testicle hormone is measured by the Cock-unit, which is the quantity of hormone, dissolved in 0·5 ccm. of sesame oil and injected into a cock causes an increase of 20 per cent in the size of its comb. This hormone, like that of the follicle, is continually fed on to the blood stream.

Similar to the follicle hormone group, the testicle hormone is also represented by a number of chemically distinct compounds called the androsterone group. Four important compounds isolated from natural sources and belonging to this group, have so far been isolated. Their names, formulæ, etc., are given below :

TABLE II.

Name.	Empirical formulæ	Source.	Quantity necessary to show an activity of 1 cock unit.
Androsterone	$C_{19}H_{30}O_2$	men's urine	200γ
Dehydro-androsterone	$C_{19}H_{28}O_2$	„ „	600γ
Androstandione	$C_{19}H_{28}O_2$	Testicles	250γ
Testosterone	$C_{19}H_{28}O_2$	„	30γ

In order to give an idea of the very low concentration of androsterone and dehydro-androsterone present in men's urine, it is only necessary to say, that about 20 mg. of the two compounds are obtained from about 100 litres of urine.

The last two compounds have only recently been isolated, androstandione by Ogata and Hirano[2] and testosterone by Laqueur[3]

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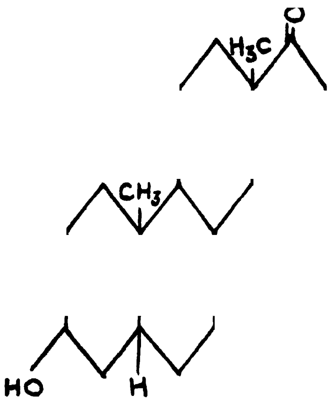
1. Nature, *133*, 377.
2 *J. Pharm. Soc. Jap. 54*, 11.
3 *Hoppe-Seylers Z.*, *233*, 281.

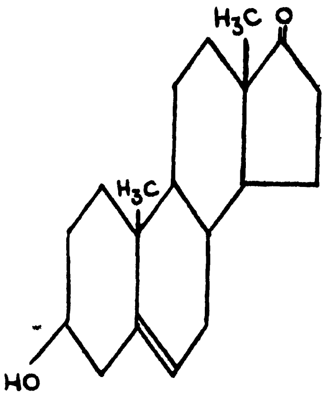
from the extract of testicles, where they are present in extremely small quantities.

Qualitatively all these compounds are very similar to each other in their physiological action, but quantitatively they vary considerably, depending upon the particular animal chosen and the particular test employed. Even the solvent seems to be of great importance in determining the activity of the individual substances and Miescher[1] has shown, that different fatty acids raise or lower the activity of the members of the androsterone group.

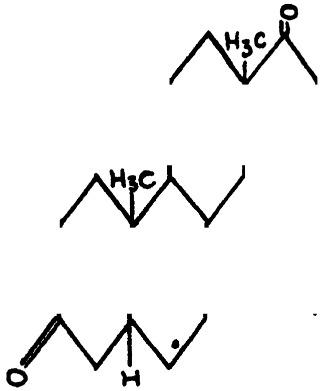
The chemical constitution of these four substances is given below :



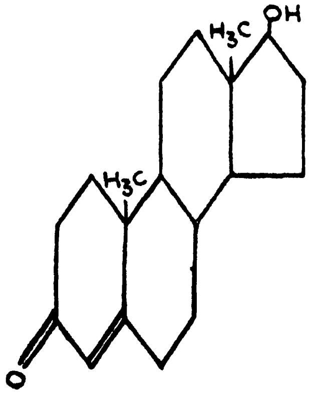
1. ANDROSTERONE



2. DEHYDROANDROSTERONE



3. ANDROSTANDIONE



4. TESTOSTERONE

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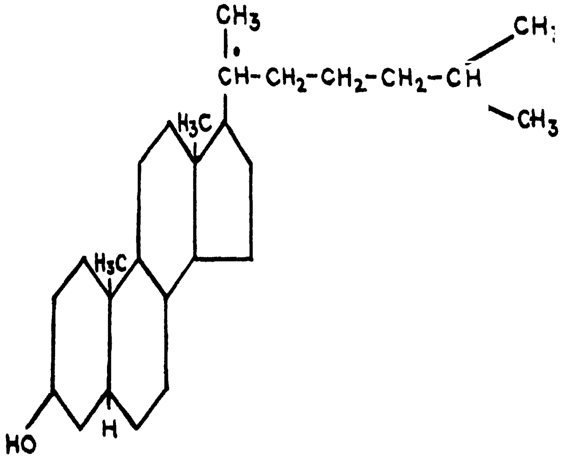
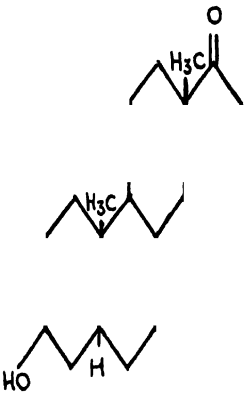
[1] *Schweiz. med. Wochenschr., 1936,* 310.

It is remarkable, that even though the oestrone group and the androsterone group are physiologically so entirely different in their action, the same four ring system is common to them and that chemically the two groups are closely related to each other. In fact, it has been shown by Schoeller and his co-workers[1] that the reduction of oestrone results in the addition of 8 hydrogen atoms and the octahydro-oestrone so obtained has, qualitatively, the same physiological action as androsterone. Thus the typically female hormone can, by means of the simple action of a reducing agent, be transformed into a typically male hormone! Butenandt has suggested, that these hormones are formed in the body by the oxidation of the side chain in the sterine molecule. Ruzicka[2] has gone a step further and actually obtained androsterone synthetically from epi-dihydro-cholesterine by oxidising it with chromic acid anhydride:



EPI-DIHYDRO-CHOLESTERINE



ANDROSTERONE

Shortly afterwards, Schoeller, Serini[3] and others as also Ruzicka. Oppenauer, Fernhold and Butenandt[4] succeeded in getting dehydro-androsterone from cholesterine by a similar reaction.

The discovery of testosterone is due to the fact, that testicle extract was found to be considerably more active in causing the

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1. *Naturwiss, 21,* 286.
2. *Helv. Chim. Acta, 17,* 1395.
3. *Naturwiss, 23,* 337.
4. *Naturwiss, 24,* 535.

growth of vesicular glands of infantile rats than even pure androsterone. This led to the surmise that the extract contained some other more active hormone and in June 1935, Laqueur[1] announced the isolation of testosterone. Soon afterwards Hanisch[2] and Wettstein[3] independently succeeded in synthesizing this substance and proving its constitution as shown above. Its synthesis from and resterone would justify the name androstenelone to the same and it is therefore also fairly easily obtainable from cholesterine.

We now come to the consideration of the third type of sex hormone, the hormone of the corpus luteum. It is specific in its physiological action and is dissimilar to the two types already described above. The corpus luteum is normally present in the ovaries of the woman only in the second half of the menstrual cycle and the hormone secreted by it is thus present when the quantity of the follicle hormone has diminished to a considerable extent. The function of this hormone seems to be to fit the uterus for eventual pregnancy. If the discharged ovum is fertilised, the corpus luteum remains intact and a further quantity of the hormone secreted by it is formed in the placenta, which then appears to take up the function of maintaining the pregnancy, keeping the uterus at rest and preparing the breast glands for lactation.

As a test for this hormone is used the transformation of the mucous membrane of the uterus of a guinea pig. The isolation of the hormone of corpus luteum was successfully accomplished by Butenandt, Westphal and Hohlweg,[4] by Slotta and Fels,[5] by Allen and Wintersteiner[6] and by Hartman and Wettstein[7] independently of each other and more or less simultaneously in 1934. From 100 Kg. of pigs' ovaries about 50 mg. of the pure hormone, called progesterone, could be prepared.

In contrast to the oestrone and androsterone groups, progesterone is the only representative of this class, although it has been shown to exist in two crystalline modifications, one melting at 121° and the other at 128°.

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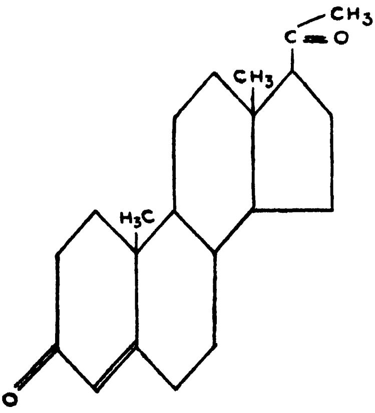
1. *Loc. cit.*
2. *Ber, dtsch. chem. Ges.*, *68*, 1859.
3. *Helv. Chim. Acta*, *18*, 1264.
4. *Hoppe-Seylers Z.*, *227*, 84.
5. *Ber. dtsch. chem. Ges.*, *67*, 1270, 1624.
6. *Journ. Biol. Chem.*, *207*, 321.
7. *Helv. Chim. Acta.*, *17*, 878.

Progesterone is a simple unsaturated tetracylic diketone of the formula $C_{21}H_{30}O_2$. Its structure is represented as follows :



PROGESTERONE

It will therefore be seen, that all these three groups of hormones, with more or less entirely different physiological action, are derived from the same four ring system, the difference in action being due only to the chemical nature of the substituents and their position in the molecule.

In addition to the above naturally occurring hormones, the chemical constitution of which has been accurately established, a large number of derivatives of these have been prepared in the laboratory and it has been observed, that physiological action persists in a great majority of these compounds. Curiously enough, a number of hydrocarbone, *e.g.*, 1 : 2 : 5 : 6-dibenzanthracene, which are very similar in their chemical constitution to the oestrone group, are also known to cause cancer in mice. We thus see that physiological growth phenomena and irregular growth of cells are closely related to each other and it is difficult to predict where new work in this field will lead us.

In the case of androsterone, the physiological action is much more directly dependent on the chemical constitution and it may even happen, that out of two stereoisomeric modifications, one has a specific hormone action while the other is inactive. In the case of progesterone also, the slightest change in the molecule destroys all specific action.

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The above are general reviews and summaries. Original papers are referred to in the text.

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CHEMISTRY OF CHLORAL AND CHLORAL HYDRATE

By

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Chloral was first prepared by Liebig (*Annalen. 1.* 189) by continuous chlorination of alcohol. Dumas (*Ann. Chim. Phys. 56.2.* 125) and Stadeler (*Annalen. 61.* 101) studied its composition. Chloral, as trichloro-acetaldehyde, should have been obtained by the Chlorination of acetaldehyde, but butyl-chloral, instead, is the product, unless water and calcium carbonate are used to neutralise the hydrogen chloride that is produced: A. Pinner (*Ber. 4.* 256).

Chloral is manufactured on a large scale from chlorine and alcohol. The process is divided into two stages: (1) the preparation of chloral alcoholate and (2) its conversion into chloral. Chlorine is passed into dehydrated alcohol with crystalline ferric chloride as a catalyst (*Page. Annalen.* 1884. *225.* 209) keeping the reaction-mixture cooled at first, which is then heated to 60° and further to 100° until it becomes soluble in water. The reaction is vigorous at first and then slows down. On cooling, a white mass of chloral alcoholate is obtained. This alcoholate, when decomposed with sulphuric acid, gives chloral, which is then purified by redistillation. Chloral, which is a liquid, is then added to a theoretically calculated quantity of water and the product of the reaction, when poured over a smooth surface, solidifies. This solid is chloral hydrate. A latest method for the manufacture of chloral has been described by P. Durocher (*La. Nature.* 1926. *54.* (*1*) 81-83.)

The importance of chloral and its derivatives is twofold: (1) their physiological properties and (2) the wide range of their chemical reactivity.

The investigation of its physiological properties was first undertaken by O. Liebrich (*Ber. 2.* 269), and for a long time, there was controversy as to how it acted in the system. Liebrich was of opinion that it reacted in the system after having decomposed into chloroform. This opinion has been systematically opposed by many amongst whom are A. Tomaszewiez (*Pfluger's Archiev, fur physiologie. ix* 35-43) and A. Kast (*Zeit, Physiologie, Chem. 11,* 277-285).

Chloral has been also found to be a hypnotic and an antipyretic. (E. Harnack and J. Ramertz. *Chem. Centr*. 1893. *1*. 841-842). Its action on heart has been studied by E. Rhode (*Chem. Centr*. 1905. *2*. 1544).

Amongst various other compounds of chloral, found useful physiologically, those that are obtained by the condensation of chloral with acid amides show special interest. Of the chloralamides, chloral formamide has been investigated and has been found to be superior to chloral or to chloral hydrate as a hypnotic and is of most value in cases of nervous insomnia and similar disorders (Hagner and Hubner, *Weiner. med. Presse*. 1899, 1361). It has no corroding action, does not affect digestion, nor disturbs the heart. (*Merck's Bull*. 1899, 85).

Turning to its chemical importance, the vast range of compounds obtained in the literature suggests that chloral is almost universally reactive. It reacts with hydrocarbons, phenols, alcohols, acids, various bases, as also with reagents like hydrogen sulphide, halogens, phosphorus halides, acid chlorides, sulphuric acid, cyanides and cyanates, and oxidising agents. Its various reactions can be classified as follows :

(1) Condensation with hydrocarbons.
(2) ” ” alcohols.
(3) ” ” aldehydes.
(4) ” ” ketones.
(5) ” ” carbohydrates.
(6) ” ” phenols.
(7) ” ” bases.
(8) ” ” acids.
(9) ” ” amido compounds.
(10) Miscellaneous reactions.

(1) Condensation with Hydrocarbons.

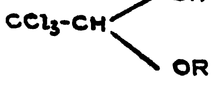
Hydrocarbons like benzene, toluene, and xylene condense with chloral, either alone or in the presence of condensing agents such as sulphuric acid, aluminium chloride etc., and give different products. Thus benzene and chloral gave diphenyl trichloroethane ; $(C_6H_5)_2CHCCl_3$ (A. Bayer, *Ber*. 1872. *5*. 1089 ; 1873. 6. 220 ; G. Goldschmidt. *ibid*. *6*. 985). O. Zeidler (*Ber*. 1874. *7*. 1180) condensed bromo and chlorobenzenes with chloral in the presence of sulphuric acid and obtained the product similar to above : $(C_6H_4Cl)_2CHCCl_3$. These compounds when treated with boiling alcoholic potash lose hydrogen chloride and are turned to $(C_6H_5)_2C{=}CCl_2$. (G. Goldschmidt *loc. cit.* ; O. Zeidler. *loc. cit.*). The compounds identical with those described above have also been obtained with aluminium chloride as a catalyst by Mark Van Laer (*Bull. Chim. Belg.* 1919. *28.* 346-350). Harris and Frankforter (*J. Am. Chem. Soc.* 1926. *48.* 3144) say that the condensation of the halogen substituted aldehydes with hydrocarbons gives quantitative results.

With aluminium chloride as a condensing agent, chloral hydrocarbons have been obtained, where one molecule of chloral has condensed with one molecule of hydrocarbon. Thus with benzene, Phenyl--trichloro-methyl-carbinol; with toluene, p-tolyl-trichloro-methyl carbinol; with xylene, p-xylyl-trichloro-methyl carbinol have been obtained by A. Dinesmann (*Compt. rend.* 1905, *141,* 201-203). Chattaway and Muir (*J.* 1934. 701) condensed benzene with chloral hydrate in presence of conc. sulphuric acid and obtained β-trichloro-α-phenyl-ethyl-carbinol. When carbon disusphide was used as a medium in the above experiment, tetraphenyl-ethane, diphenyl dichloroethane triphenyl-vinyl-alochol and some other hydrocarbons were obtained. (H. Biltz *Ber. 26,* 1952). Dinaphthyl-trichlor-ethane $(C_{10}H_7)_2CH \cdot CCl_3$ was obtained by Grabowski (*Ber. 6,* 224-225) from chloral and naphthalene in sulphuric acid. These trichlor-ethane-compounds of Hydrocarbons $(R_2CH \cdot CCl_3)$ change to dichlor-ethylene compounds $(R_2C : CCl_2)$ on boiling with alcoholic potash . (Grabowski & Beyer, *loc. cit.*)

(2) Condensation with Alcohols.

Chloral condenses normally with alcohols to give the alcoholates

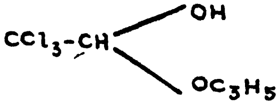
of the type :



$CCl_3\text{-}CH\begin{cases}OH\\OR\end{cases}$

Chloral and absolute alcohol give chloral ethylate (Martius and Mendelsohn. *Ber. 3,* 444) ; Emille Gallenti (*Gazetta* 1901. *31,* 86-92) and Victoria (*Chem. Soc. Abst.* 1905. 110) obtained chlorol propylate and chloral isopropylate from propyl and isopropyl alcohol respectively; chloral and amyl alcohol give chloral amylate (*Gadamer. Arch Pharm. 243,* 30; Kelle & Co., D. R. P. 115251; *Chim. Zentr.* 1900. *2.* 1141) A. Oglialoro (*Gaz. Chim.* 1874. 463) obtained chloral

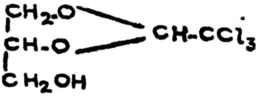
allylate



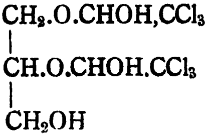
$CCl_3\text{-}CH\begin{cases}OH\\OC_3H_5\end{cases}$

from allyl alcohol. De Foreranda (*Comp. rend.* 108, 618-620) obtained chloral glycollate and chloral glycerolate from glycol and glycerol respectively. Meldrum and Vad (*J. Ind. Chem. Soc.*

1936. *13*. 118) also studied the condensation of chloral with glycerol, when with one molecule they obtained

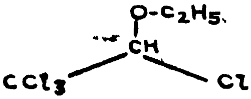


and with two molecules.



$$\begin{array}{l} CH_2.O.CHOH,CCl_3 \\ | \\ CH.O.CHOH.CCl_3 \\ | \\ CH_2OH \end{array}$$

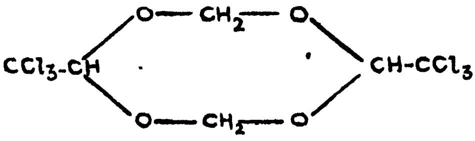
Some more alcoholates were studied by Jacobson (*Am. Ch. Pharm.* 157, 243.) and by Kuntze (*Arch. Pharm.* 246, 91). Chloral borneolate has been obtained by Haller (*Comp. rend. 112,* 143), also mentholate and terpinolate by Wagnitz (Eng. Pat. 19103 ; *J. C. S. Ind.* 1899. 856) and by Schmidt (*Comp. rend. soc. Biol.* 1890. 678). These chloral alcoholates are not the molecular compounds but real ones, is shown by L. Henry (*Ber.* 1871. 101) who reacted chloral ethylate with phosphorous pentachloride and obtained



It is interesting to note that aliphatic alcohols react with chloral while aromatic do not.

(3) Condensation with Aldehydes.

With aldehydes, an aldol type of condensation takes place. Thus from chloral and paraldehyde, W. Koenigs (*Ber. 25*. 792-802) obtained chloral aldol and from butyl chloral, paraldehyde-butylchloral. A. Pinner (*Ber.* 1898. *31,* 1926) condensed formaldehyde with chloral in the presence of sulphuric acid and obtained hexachloro-dimethyl tetroxan :



(4) Condensation with Ketones.

Chloral acetone : CCl_3. CH(OH). CH_2 $COCH_3$ is obtained by condensing chloral with acetone in acetic acid, and chloral acetophenone : $CCl_3.CH(OH)CH_2.CO.C_6H_5$ from acetophenone, (W. Koenig. *loc. cit.* ; Gigli. *Gaz. chim. ital. 28. 2.* 83 ; Wislicenus, Kircheisen, and Sattler. *Ber.* 1893, 908). Acetylacetone chloral, benzoylacetone chloral, and benzoyl acetoneoxime chloral have also been obtained by *Gigli* (*loc. cit.*)

(5) Condensation with Carbohydrates.

A study of the reaction of chloral on glucose (A. Heffter, *Ber. 22.* 1050-1051) and that on cellulose, starch and glucose (Ross and Payne. *J. Am. Chem. Soc.* 1923. *45.* 2363-2366) has revealed that glucose gives two isomeric chloraloses of the formula $C_8H_{11}O_6Cl_3$. Hanriot condensed chloral in presence of hydrochloric acid, with arabinose and xylose (*Comp. rend.* 1895, *120.* 153-55), galactose and levulose (*ibid.* 1896. *122.* 2127) to respective chloraloses. Arabinobromolose (*Ann. Chim. Phys.* 1901. *8. 18.* 466) was also obtained by him. Chloralic acid is obtained by oxidation of a Chloralose. Cellulose and starch do not give the corresponding chloral derivatives, but dichloral glucoses which are also obtained from chloral and glucose (Ross and Payne. *loc. cit.*).

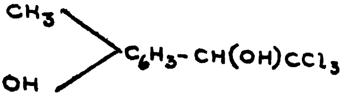
Hanriot and his associates have studied chloral derivatives of various carbohydrates (Hanriot & Richet, *Compt. Rend.*, 1892, *116,* 63 ; 1893, *117,* 734 ; 1896, *122,* 1127 ; *Bull, soc., chim.* 1893, *9* (3), 947 ; 1894, *11* (3), 37, 258, 303. Hanriot ; *Ann., chim., Phys.*, 1909, *18,* 466. Hanriot & Kling, *Compt. Rend.* 1911, *152,* 1398, 1596 ; 1913, *156,* 1380. Meunier, *Ann. chim. Phys.* 1906, *22*(*6*), 413. Petit & Polonawski, *Bull. soc. chim.* 1894, *11*(*3*), 125 ; Pietet & Richel, *Helv. chim. Acata,* 1923, *6,* 621).

Hanriot, Polonwaski and Pietet and Richel have assigned separate structures to β-glucochloralose. Since this compound condenses further, according to Coles, Good Hue, Hixon and White, (*J. Am. Chem. Soc.*, 1929, *51,* 519 ; 1930, 52, 3191) none of these formulae is satisfactory.

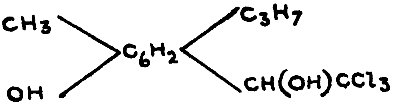
(6) Condensation with Phenols.

Chloral generally condenses with phenols in the nucleus, either one molecule, or two. It also condenses with the-OH group. In the nucleus, chloral condenses with phenols to give trichloro-methyl-carbinol derivatives. Anhydrous potassium carbonate has been used as a condensing agent. Thus Pauly and Heinrich Schanz (*Ber. 56.B.* 979-985) obtained p-hydroxy-phenyltrichloro-methyl-carbinol ; 3-methoxy-4-hydroxy-phenyl-trichloro-methyl-carbinol and 2 : 3 or 3 : 4-dihydroxy-phenyl-trichloro-methyl carbinol.

Mazzara (*Gazzetta, 13*. 269-272) condensed p-cresol and thymol with chloral and obtained p-cresol-chloral :



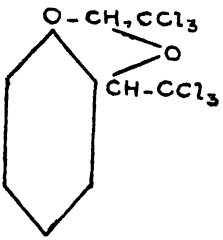
and thymol-chloral :



respectively.

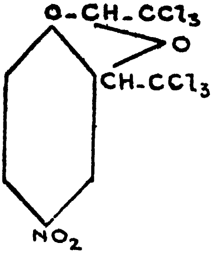
Condensation of chloral with resorcinol has been studied by Causse (*J. C. S.* 1886. 1020 ; *Comp. rend. 103* 347-350) and by Hewitt and Pope (*Chem. Soc. Trans.* 1896. 1265 ; 1897-1084).

Condensation of phenol and thymol with chloral has been studied by Meer (*Ber. 7*. 1200-1203) in the presence of sulphuric acid and acetic acid. The condensation is nuclear and of the type CCl_3. CH. $(C_6H_4OH)_2$. Hinsberg (D. R. P. 332678 ; *Chem. Zentra.* 1921, ii, 648) has condensed chloral with p-acetyl-amino-phenol with the result that he obtained a compound : CCl_3. CH(OH). O. C_6H_4. NH. Ac. It decomposes on sudden heating and gives out chloral vapours ; yields chloral when boiled with water. It is more energetic soporific than chloral. Chattaway and collaborators (*J. C. S.* 1926. 2720 ; 1928. 1088. 2913) have still further condensed chloral in such a way that one molecule of chloral condenses in the nucleus in ortho-position to -OH, while the other with -OH group, with a further formation of an anhydro structure of the type :



Thus Chattaway and Morris (*Coc.* 1927. 2013-2017) obtained anhydro-2- β-trichloro- α-hydroxyethoxy-1- β-trichloro- α-hydroxy-ethyl-benzene-5-sulphonic acid, by treating phenol dissolved in cold sulphuric acid, with chloral hydrate ; and anhydro-5-nitro-2- β-trichloro- α-hydroxy-ethoxy-1- β-trichloro α-hydroxy-ethyl-benzene ;

from p-nitrophenol.

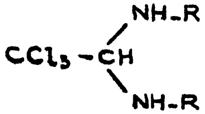


Chattaway and Calvet (Annals. Phis. Quim. 1928. *26*. 75-91) on condensing p-amino-phenol with chloral, obtained anhydro-5-amino-2- β-trichloro- α-hydroxyethoxy-1- β-trichloro- α-hydroxy-ethyl-benzene.

p-Toluene azophenol, 4-nitro-m-crseol, p-nitro-anisol and 2 : 6-dichloro-quinol have also been condensed by Chattaway and Calvet (*loc. cit.*).

(7) Condensation with Bases.

Chloral acts violently with bases like aniline, toluidine (O. Wallach. *Ber*. *4*. 668-669). The resulting compounds are basic in nature (Wallach. *loc. cit.*) and give hydrochlorides and chloroplatinates (D. Amato. *Gaz. Chim. Haliana*. *5*. 461-467). With aniline, toluidine and xylidine, O. Wallach (*Annalen*. *173*. 274-288) obtained compounds of the type :



$$CCl_3-CH\begin{cases}NH-R\\NH-R\end{cases}$$

A similar compound has been obtained, with o-toluidine by Wheeler and Jordan (*J. Am. Soc*. 1908. *30*. 136-142). Wheeler with collaborators obtained the same type of compounds with brom-anilines, nitranilines and anisidines. With Miller (*loc. cit.*) he obtained trichloro-ethylidine-di-p-bromaniline : CCl_8. CH. $(NH.C_6H_4Br)_2$, with Dickson (*loc. cit.*) trichloro-ethylidine-o-methoxy-phenyl-amine : CCl_3. CH(NH. C_6H_4. $OMe)_2$ and trichloro-ethylidine-p-methoxy-phenyl-amine. With Jordan (*loc. cit.*) he obtained trichloro-ethylidine-di-*m*-bromaniline. With Weller (*J. Am. Chem. Soc*. 1902. *24*. 1063-1066) he obtained trichloro-ethylidine-di-(o, m, p)-nitranilines by heating the o, m, and p-nitranilines with chloral in benzene solution. With phenylene diamines, toludines, and napthylamines (Leopold Righemer ,*Ber*. 1906. *39*. 1653) obtained compounds of the type CCl_8. CHOH. NH. R. NH_2. By triturating chloral hydrate and sodium carbonate with hydroxylamine hydrochloride, Hantzch (*Ber.* *25.* 701-705) obtained chloral-hydroxylamine. Amino-pyridine has also been condensed with chloral by Schmidt and Becker (*Monat.* 1926. *46.* 675-678). With 2 : 4-dimethyl quinolene, Spallino and Cucchiaroni (*Gazzetta,* 1912. *42.* 517-525) obtained condensation with the side alkyl group and the product was 4-methyl-2 trichloro-propenyl-quinoline :

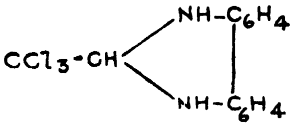
While Koenigs and Mengel (*Ber.* 1904. *37.* 1322-1337) obtained a nuclear product namely chloral-2 : 4-dimethyl quinoline ; and chloral-2 : 4 : 6-trimethyl piperidine from 2 : 4 : 6-trimethyl piperidine. Antipyrine gives chloral antipyrine and dichloral antipyrine (Behal and Chody. *Ann.* *Chim.* *Phys.* *2766.* 319-339).

With substituted amines, Chloral condenses in the nucleus. Thus Bosseneck (*Ber.* 1885. *18.* 1519 ; 1886. *19.* 365 ; 1887. *20.* 3193 ; 1888. *21.* 782) condensed chloral with dimethylaniline, diethylaniline, monomethylaniline and monoethylaniline. Meldrum and Datar (*Proc. Ind. Acad, Sci.* 1935. *2.* 580) have also condensed substituted anilines with chloral according to Bosseneck, with some modifications, with a view to study the reduction of CH(OH). CCl$_3$ group.

Chloral has also been condensed with methyl and ethyl o-toluidines by Meldrum and Advani (*J. Ind. Chem. Soc.* 1933. *10.* 107-110), thus getting p-(β-trichloro-α-hydroxyethyl)-methyl-o-toluidine and p-(β-trichloro-α-hydroxyethyl)-ethyl-o-toluidine.

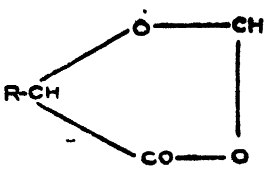
2 : 4-dihalogen substituted phenylhydrazines react smoothly with chloral giving 2 : 4-dihalogen substituted phenylhydrazones of the corresponding glyoxalates (Chattaway and Bennett. *Soc.* 1927, 2850-2853).

Weiss and Chledowski (*Monatsh.* 1935. *65.* 357) obtained cyclic compounds from diamides and chlorals. Thus o-o'-diamino-diphenyl and chloral gave :

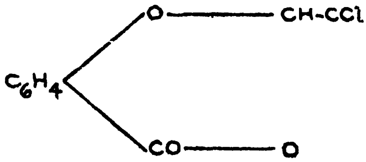


(8) Condensation with acids.

Chloral acts on acids in various ways. α-hydroxy acids give chloralides of the general formula



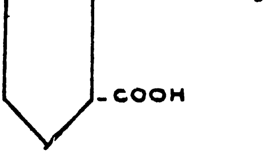
These chloralides have interested a number of workers. Stadeler (A. 1847, *61* 101 ; 1858 *106*. 254 ; Wallach. *ibid.*, 1878. 193, 1 ; Otto. *ibid*. 1888. *239*. 262 ; Kekole, *ibid*. 1858. *105*. 293 ; Grabousky. *Ber*. 1873. *6*. 255. 1070 ; 1875. *8*. 1433 ; Schiff, *ibid.*, 1898. *31*. 1898 ; Edeleanu and Zacharia. *Chem*. *Zentr*. 1895. 2. 212 ; *Patterson and Macmillan J. C. S.*, 1921. *101*. 794 ; Boeseken, *Proc. K. Akad. Wetensch Amsterdam*, 1926, *35*. 1084). Wallach (*Loc. cit.*) prepared these chloralides by heating the reacting substances in a sealed tube. The yields he obtained were thus not satisfactory. Meldrum & Bhatt (*J. Bom. Uni.*, 1934, *3*, 149) improved upon Wallach's method and obtained chloralides in good yields by carrying out the reaction with chloral hydrate at room temperature in the presence of sulphuric acid. Boeseken (*Proc. K. Akad. Wetensch. Amsterdam*, 1927, *30*. 55) and Yorston (*Rec. Trav. Chim*, 1927, *46*, 711) had used this method before. It works satisfactorily with aliphatic acids, (Yield abt. 80%), but not so with aromatic acids and fails with benzilic acid. Shah & Alimchandani later (*J. Ind. Chem. Soc.*, 1934, *11*, 545) prepared chloralides according to Meldrum and Bhatt (*loc. cit*) with a view to study their reduction with zinc and acetic acid. According to them heating in a sealed tube (Wallach, *loc. cit*) is necessary for aromatic acids. O. Wallach has also mentioned a choralide of salycylic acid.



(*loc. cit.*) which he obtained in a very small quantity, but Alimchandani, Shah and Deo (*Current Science*, 1934, *3*, 354) did not get any such chloralide, having tried under different conditions, and even with different substituents in the salicylic acid nucleus (*J. Ind. Chem. Soc.*, 1936, *13*, 354). Shah and Alimchandani have also studied isomerism in chloralides (*Current Science*, 1934 *2*, 383) and their reduction with zinc and acetic acid (*Jour. Univ. Bombay*, 1936, *5*, 132).

Fittig and Miller (*Annalen*, 1889, *255*, 43) obtained trichloromethyl-paraconic acid by condensing chloral with sodium succinate in acetic anhydride. Meldrum and Kotwal (*J. Ind. Chem Soc.*, 1936, *13*, 213) obtained the same paraconic acid from chloral and succinic acid with a view to study its reduction. Lately Cavet and Mejuto (*J. Chem. Soc.*, 1936, [illegible] condensed chloral with salicylic acid, in the nucleus. Later they converted the CH (OH) Cl_3 group to COOH group. The condensation with methoxy benzoic acids was studied by Fritsch (*Annalen*, 1897, *296*, 358 ; 1898, *301*, 360), Meldrum (*Soc.*, 1911, *99*, 1712), Mollina and Bergellini (*Atti. R. Accad. Lincei*, 1912, *21* (*2*), 146) ; Meldrum and Alimchandani (*Soc.* 1920, *117*, 964). Chattaway and Pratt (*Soc.*, 1927, 685-692) condensed p-hydroxy benzoic acid with chloral and obtained anhydro 4- carboxy-2- β-trichloro- α-hydroxyethoxy-1- β-trichloro- α-hydroxy ethylbenzene. Chattaway and Calvet (*Soc.* 1928, 2913) condensed chloral with anisic acid and obtained a compound containing the group—$CHOH.CCl_3$ or — —$CHCl. CCl_3$. Meldrum and Hurry (*J. Ind. Chem. Soc.*, 1934, *11*, 535) studied the condensations of methylethers of the isomeric hydroxy benzoic acids with chloral and obtained nuclear condensation compounds. Meldrum extended this research of his to various acids. Earlier with Alimchandani he had studied condensations with methylethers of gallic acid (*loc. cit.*) and with gallic acid and cresotic acids (*Soc.*, 1921, 119, 201). It was continued later by Alimchandani with Shah (*J. Ind. C.S.*, 1931, *8*, 261) who showed that (*J. Ind. Chem. Soc.*, 1925. *2*. 1 ; 1929 *6*, 253), it is the α-coccinic acid and not the τ coccinic acid (Schleussaer and Voswinckel, *Ann*, 1921, *422*, 111) that is obtained through the condensation of chloral with m-cresotic acid. With (Miss) Katrak, he (*J. Ind. Chem. Soc.*, 1932, *9*, 121-125) studied the condensation of butyl chloral with gallic acid and three cresotic acids ; and with Kapadia (*J. Ind. Chem. Soc.*, 1932, *9*, 483) the condensation of chloral with 2-hydroxy-p-toluic acid and its methyl ether. An important synthesis of phenylacetic acid derivatives was achieved by Meldrum and Parikh (*Proc. Ind. Acad. Sci.*, 1935, *1*, 431-436) through the condensation of chloral with gallic acid and its methyl derivatives. Credit of the synthesis of m-hemipinic acid is also due to the same authors. The synthesis of β and τ—coccinic acids and then of cochinilic acid by the condensation of chloral with 5-hydroxy-m-toluic acid Meldrum and Vaidyanathan (*Proc. Indi. Acad. Sci.*, 1935, *1*, 510-527) has raised the importance of these researches still further.

Anthranilic acid has been condensed with chloral to form chloral dianthranilic acid : $CCl_3. CH. (NH. C_6H_5 COOH_2)$ (Niementowski , *Ber.*, 1902, *35*, 3898) It has also been condensed with chloral (*Ber*, 1895, *28*, 2812 ; *J. Am. C. S.*, 1908, *30*, 139) and the compound



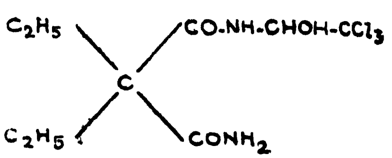
has been obtained.

(9) Condensation with Amido Compounds.

Chloral condenses with the—NH_2 group of the acid amides and generally gives compounds of the type:

$$R. CO. NH. CH. (OH) CCl_3$$

Thus Oscar Jacobson (*An. Chem. Pharm.*, 157, 243) prepared chloral-acetamide and chloralbenzamide; O. Wallach (*Ber.*, 5, 251-257) also prepared the same compounds. Chloralformamide was prepared by J. E. Mering (Eng. Pat. 7391; D. R. P. 505886; *J. C. S. Ind.*, 1890, 413). It was also prepared and its physiological properties studied in Merck's laboratories (*Merck's Bull.*, 1889, 85). Chloral-palmitinamide and chloral-bromopalmitinamide have been obtained by Sulzberger (D. R. P. 198715) and chloral-bromo-isovalerimide by Richter (Chemisch. Fabrik. D. R. P. 234741). Meldrum and Bhojraj (*J. Ind. Chem. Soc.*, 1936, *13*, 185) prepared various chloralamides ranging from chloralformamide to chloral pelargonamide. Meldrum and Deodhar (*J. Ind. Chem. Soc.*, 1934, *11*, 529-533) studied the chloralamides of succinic, malonic and p-toluic acids. Wheeler and Yelburgi (*J. Ind. Chem. Soc.*, 1934, *11*, 217-223) prepared chloral acetamide and chloralbenzamide with a view to study the constitution of their reduction products, which they have shown to be unsaturated; represented by the formula: $R.CO.NH.CH. = CCl_2$ Only one molecule of chloral has been condensed with diethyl malonamide to give



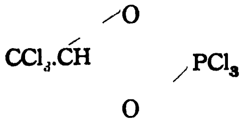
(Burrows and Keane, *Soc.*, 1907, 271).

Chloral with cyanamide gives $(CN)_3$. $(NH. CH. OH. CCl_3)_3$ Fillet and Schiff (*Ber.*, *10*, 425-429). Condensation of urea also takes place on the same lines as that of the amides and chloral (O. Jacobsen *loc. cit*); Kelle and Co. (D. R. P. 128462; *Chem. Zentr.*, 1902, *1*, 547). Van der Zande (*Rec. Trav. Chim.*, *8*, 222-247) prepared a number of urea derivatives:—chloral-dimethyl-carbamide, chloral-diethyl carbamide, chloral-dipropyl carbamide and chloral-di-isopropyl-carbamide. Fiest with Nissen and Stadler (*Ber.*, 1914, 1173-1193) obtained dichloral carbamide and dichloral-thiocarbamide by heating chloral and carbamides with a little water. Carbamide, phenyl-carbamide, tolyl-carbamide and nitro-phenyl-carbamide have all been condensed with chloral by Chattaway and James (*Proc. Roy. Soc.*, 1931) and Chattaway and Lawrence (*Soc.*, 1933, 30). Chloral-urethane and chloral-di-urethane have been obtained by Diels and Sieb (*Ber.*, 1909, *42*, 4062-4072). Meldrum and Alimchandani (*J. Ind. Chem. Soc.*, 1925, *2*, 1) and Meldrum and Pandya (*Jour. Univ. Bombay*, 1937) have also studied the condensation of chloral with urea and urethane and their halogen derivatives. Chattaway and James (*J. C. S.*, 1934, 109) condensed diamides with chloral. Thus $NH_2CONH.Me$ was condensed with chloral hydrate in water to get N-methyl-N′-(β-trichloro-α-hydroxy-ethyl) carbamide. Similarly $NH_2CONALK_2$, oxamide and substituted malonamides were condensed.

(10) Miscellaneous Reactions.

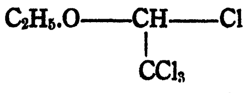
Bromine and chlorine at 140° in a sealed tube give bromo-trichloroethane with chloral (A. Oglialoro, *Gaz. Chim. Ital.*, 1874, 457-462) ; but bromine and chloral in the presence of aluminium chloride at 75-80° give hexachloroethane ; as also iodine (A. Mouneyrat, *Bull. Soc. Chim.*, 1897, *17B*, 796). Chlorine acts on chloral only in sunlight and gives carbon tetrachloride (H. Gauntiar, *Compt. Rend.*, *101*, 1161). Chloral in the presence of pyridine, sulphuric acid or aluminium chloride polymerises (Boeseken and Schimmel, *Rec. Trav. Chim.*, 1913, *32*, 112-127).

Phosphorous pentachloride acts on chloral as an aldehyde and gives $CCl_3.CHCl_2$ (E. Paterno, *Gax. Chim. Ital.*, *1*, 590-592). The action of phosphorous pentachloride on chloral also gives.



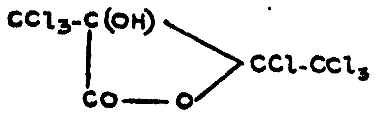
$$CCl_3.CH\begin{array}{c}\diagup O\\ \\ O\end{array}\diagup PCl_3$$

(F. Giolliti, *Gazzetta*, 1904, *34* (*1*), 247). Which is an oily liquid with pungent odour.

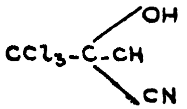


$$C_2H_5.O\text{——}\underset{\displaystyle CCl_3}{\underset{|}{CH}}\text{——}Cl$$

The production of chlor-oxyethyl-trichloro-ethylidine (above), by the action of phosphorous pentachloride on chloral alcoholate, shows that chloral hydrate or chloral alcoholate are not molecular compounds but real valency compounds (L. Henry, *Ber.*, 1871, 101). Anschutz and Haslam (*Annalen*, *253*, 121-131) have found that phosphorous pentachloride acts on chloralide and gives tetrachlorethylidene trichlorolacetate, the chloride is slowly decomposed by water yielding tri-chloro-acetic and trichloro-lactic acids. These results indicate, that the constitution of the chloride is represented by the following formula,

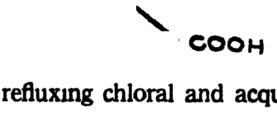


Cyanogen and chloral hydrate give cyanhydrin



$$CCl_3\text{-}C(OH)(CN)\text{-}CH$$

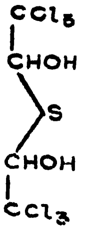
(E. Hagenmann, *Ber*, *4*, 151-154). Alcoholic potassium cyanide gives ethyl dichloroacetate and chloral cyanhydrate with chloral ; while aqueous potassium cyanide gives dichloracetic acid and hydrocyanic acid (O. Wallach, *Ber.*, *6*, 114-119). The same worker obtained dichloracetic acid with potassium ferrocyanide, (*Ber.*, *10*, 1525-1530). If potassium cyanide contains potassium cyanate as an impurity, then chloral hydrate gives a compound $C_4H_3Cl_3N_2O_2$ (Cech.. *Ber.*, *8*, 1174). He has also confirmed it further by using a mixture of potassium cyanide and cyanate (*Compt. rend.*, *82*, 989-990) and has condensed this chloral-cyanide-cyanate with toluidine giving CH_3. C_6H_4. NH.CCl_2. CHO and with ethylamine giving $C_2H_5NH.CCl_2$. CHO, (*Berr.*, *10*, 878-880) ; while O. Wallach (*Ber.*, *8*, 1327) has found that with potassium cyanate alone, chloral hydrate gives C_4H_2 $Cl_2N_2O_2$. With chloral ammonia, alcoholic potassium cyanide gives dichloracetamide (Schiff and Speciale, *Gazetta*, *9*, 335) and in the reaction chloral combines with amide to give $CHCl_2$.CONH.CHOH. CCl_3 (chloral-dichloracetamide). Chloral cyanhydrin and further an



$$CCl_3\text{-}CH(OH)(COOH)$$

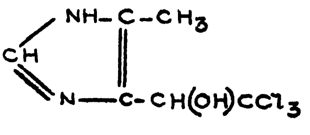
acid are obtained by refluxing chloral and acqueous hydrocyanic acid (C. Bischoff and Pinner, *Ber.*, *5*, 208). Chloral cyanhydrin condenses with carbamide and gives a simple trichiloroethylidine-diuride CCl_3. CH. $(NH.CO.NH_2)_2$ (Pinner and Litschutz, *Ber.*, *20*, 2345-2351). Chloral and hydrocyanic acid in the presence of hydrochloric acid give trichloroacetic acid and chloral cyanhydride (A. Pinner and C. Bischoff *Annalen*, *179*, 74-100 ; E. Hagemann, *Ber.*, *4*, 151-154). When hydrocyanic acid vapours are passed into chloral, trichlorinated trigenic acid is obtained (C. Bischoff, *Ber*, *5*, 86-88). This reaction according to Liebig, Wohler and Bayer, is a criterion for an aldehyde. If methyl cyanide reacts, instead of hydrocyanic acid, (Hubner, *Ber.*, 6, 109-110) oxygen of the aldehyde is eliminated as water and CCl_3 $CH.(CH_2CN)_2$ is obtained which on hydrolysis gives $CCl_3.CH.(CH_2.CO.NH_2)_2$.

If hydrogen sulphide is added to chloral hydrate, a compound of the type



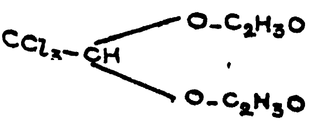
is obtained (E. Hagemann, *Ber.*, *4*, 151-154 ; G. Wyas, *Ber*, *7*, 211-212). But if hydrogen sulphide is passed through an ammoniacal solution of chloral hydrate, a red dye of the formula $C_{18}H_{24}S_{18}O_6N_4$ is obtained (Lerch., *Chem. Centr.*, 1887, 299). Chloral and fuming sulphuric acid give a compound $C_8H_6Cl_{12}O_{11}S_2$ (Grabowski, *Ber.*, *6*, 225-226) and various others (*ibid.*, *8*, 107-72)

Chloral and zinc-methyl give dimethyl-isopropyl-carbinol (Rizza, *Russ. Chem., Soc.*, 1882, 99-103). Chloral and 4-methyl-glyoxaline give



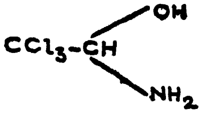
Gerngross (*Ber.*, 1912, *45*, 509-526).

Acetic anhydride, with chloral hydrate, gives a diacetyl chloral hydrate

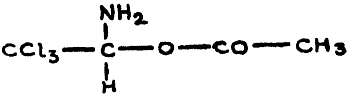


(Meyer and Dulk, *Ber.*, *4*, 963) ; while acetic acid alone gives some isomeride of chloral (Meyer, *Ber.*, *6*, 449). With corresponding chloracetic acids, chloroacetates are formed (Gabutti, *Gazetta*, 1900, *30*, 253-257).

R. Schiff (*Ber.*, *10,* 165-171) has prepared monoacetyl and diacetyl chloral ammonia by the action of acetyl chloride on chloral-ammonia. The diacetyl compound very easily hydrolyses to a mono-acetyl, simply by means of hot water. This shows that chloral-ammonia contains a hydroxyl group



From his experiment Schiff represented the formula of chloral acetamide as $CH_3.CO.NH.CH(OH).CCl_3$. A. Pinner however represented it as

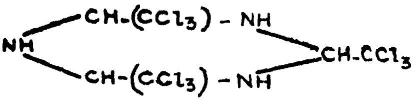


$$CCl_3—\overset{NH_2}{\underset{H}{C}}—O—CO—CH_3$$

(*Ber.*, *10,* 1964). Pinner finds support for his view, since this compound is obtained by the action of ammonia on chloral-acetyl-chloride which is represented as $CCl_3CH.Cl\ (O.C_2H_3O)$. Shiff has also condensed chloral-ammonia with benzaldehyde (*Ber.*, *11,* 2166-2167) and obtained

$C_6H_5CH : N.CH\ (OH).\ CCl_3$

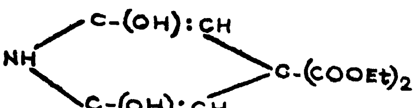
which finds to be a general reaction for aldehydes. Chloral-ammonia when distilled with chloral gives an imide



and an isochloral imide.

(Behal and Choay. *Compt., rend.*, *110,* 1270-1273).

Chloral-ammonia, with ethyl-disodiomalonate leads to the formation of a substance which is considered to be,



diethyl-2 : 6-dihydroxy-1 : 4-dihydro-pyridine-4 : 4-dicarboxylate Zwerger (Monatsch, 1903, *24,* 737).

Perusal of the above literature makes it manifest that chloral, as an aldehyde, undergoes these fundamental reactions where the doubly linked oxygen is either (*i*) converted into —OH group with the subsequent addition or (*ii*) it is eliminated as a molecule of water. Thus in the case of hydrocarbons, one molecule combines with one molecule of chloral to give

(1) $CCl_3.CHO + C_6H_6 = CCl_3.CH(OH).C_6H_5$

(2) $CCl_3.CHO + 2\ C_6H_6 = CCl_3.CH.(C_6H_5)_2$

The first type of reaction is general and is found true in cases of alcohols, aldehydes, ketones, carbohydrates, acids, amides, substituted anilines, and with bases containing nitrogen in the ring. It is interesting to note that aliphatic alcohols react with chloral, while the aromatic do not. With aromatic compounds, the reaction is generarally nuclear, unless a characteristic group such as —OH, —NH_2 or acetylamido is present. Thus with phenols, chloral condenses in the nucleus or with the —OH group or with both. If chloral condenses in the ortho position to —OH group with an additional molecule condensing with —OH group, an anhydro compound is obtained with elimination of a molecule of water from these two chains. Compounds of this type have been obtained by Chattaway and his collaborators from various phenols.

Alimchandani and Meldrum also had obtained similar anhydroderivatives from gallic and other hydroxy acids. With aliphatic hydroxy acids, Wallach has obtained compounds which he calls 'chloralides,' and these are also anhydro formations.

With hydroxy aromatic acids, chloral condensation takes place in the nucleus as usual, but if the condensation takes place in the ortho position to the —COOH group, or in the ortho position to the —OH group in the case of hydroxy acids, then a phthalide is obtained. This speaks of the reactivity of the —OH group in the chloral condensation.

The nuclear condensation of chloral with aromatic acids, has been used by Meldrum and his collaborators to get many interesting compounds. They have arrived at these through the following stages :

(*i*) Condensation of chloral to get
$R.\ CH(OH).CCl_3$.

(*ii*) Reduction of this to get
$R.\ CH_2.CHCl_2$.

(*iii*) Reaction of sulphuric acid (97%) on this to convert
$R.CH_2.CHCl_2$ to $R.CH_2.COOH$.

However, the reaction is not general. The necessary condition for this type of condensation appears to be the presence of a para-activating group.

In the case of amino compounds, chloral generally condenses with the —NH_2 group in the second way. Thus two molecules of amine with one of chloral give

$$CCl_3CHO + 2NH_2.C_6H_5 = CCl_3CH.\ (NH.C_6H_5)_2$$

but if the basic group is substituted, as in the case of diethyl or dimethyl aniline, chloral condenses in the nucleus and the condensation is of the first type. With acid amides, chloral condenses with the amido group and chloralamides are formed. No acid amide is known where chloral has combined in the nucleus. Aliphatic as well as aromatic acid amides, urea and urethanes have all been condensed with chloral. These chloralamides have been found to be very useful in medicine. In order to enhance their therapeutic efficiency, a number of reactions have been tried by Moscheles, Pinner, Feist and others. All these reactions have centred round the —OH group in the side chain ; and that —OH group can be exchanged for many other groups such as —OCH_3 ; —COCH ; COC_6H_5 ; Cl ; Br., etc., has been shown by them.

The Author and his students are interested in the study of the chloral amides in general and that of the chloral-salicylamides in particular, because of their potential therapeutic importance since both salicylic acid and chloral, with their derivatives are important amongst drugs. Further study of these compounds, besides, may lead to important syntheses of hetero-cyclic substances

[*Received August 11, 1937.*]

ABSTRACTS OF THESES

I.—*Charge of Cloud Drops and Solid Particles produced* By MECHANICAL METHODS AND THE THEORY OF ITS PRODUCTION : R. D. Godbole, Royal Institute of Science, Bombay.

Experiments were carried out with various substances to find out the charge in the substances when these are subjected to mechanical processes such as spraying a single jet, striking a plate, two jets striking each other, slipping on an inclined plane, etc. Substances contained pure liquid solutions of organic and inorganic substances and powders. A jet of gas such as CO_2 was made to strike a plate and the charge produced was measured. In certain cases, the charge given to the air as well as in the substance was determined. When the charge of one kind was not found either in the substances or in air, special experiments were arranged with insulated sprayer to find out the missing charge. These show that some of the charge escapes through the apparatus to the earth.

The experiments of the author and previous workers like Lenard, Eve, Busse, Simpson and Rudge lead to the following general results :

(1) The charge in the substance, in the surrounding medium and that escaping through the apparatus is in total zero.

(2) If the substance is positively charged, an excess of negative ions over positive ions is found in air in general and vice versa. The missing charge, if any, escapes to the earth through the apparatus. Negligible charge in the substance is accompanied by a negligible charge in air also.

(3) The nature and amount of charge produced, depends upon the intensity of the mechanical action as well as on the state and the nature of the substance.

Experiments were also conducted with substances initially charged and then subjected to mechanical action. These show that the charge due to mechanical actions is independent of the initial charge. The initial charge remains in the liquid and is not given to the medium when the substance is subjected to mechanical action.

AUTHOR

II.—*Measurement of Earth-Air Electric-Current* : D. V. KAMAT, Royal Institute of Science, Bombay.

An automatic apparatus as suggested by G. C. Simpson and as put to use by Seraje at the Kew Observatory, was set up for taking continuous records of the earth-air current, in the compound of the Meteorological office, Poona. Continuous records of the current and the potential gradient were simultaneously obtained for 11 months of the year, and these were analysed for diurnal and other variations. The general conclusions that follow from these analyses are :

(1) The potential gradient at Poona, frequently becomes negative even in fair weather, while the earth-air current maintains the usual positive sign ; this is mostly because of the space charge due to the dust in the atmosphere. Therefore, the relation between the earth-air current i, the conductivity λ and the earth-air-current F, in this case is of the form $i = \lambda (F + Fo)$. The additional term λFo arises on account of this space charge and some special records are analysed for finding the values of Fo.

(2) For studying the diurnal and other variations of the electrical elements portions of the records of positive values of the earth-air-current and the potential gradient obtained during the undisturbed conditions only, are taken into account. From these analyses, it is seen that :—

(*a*) The potential gradient assumes the usual form consisting of two distinct maxima and two minima.

(*b*) The variations of the current and the conductivity are very much similar to each other.

(*c*) The variation of the conductivity is, more, or less in the direction opposite to that of the potential gradient.

(*d*) The current and consequently the conductivity are maximum in the summer and the monsoon months and minimum in the winter months. But the potential gradient is minimum in the summer and the monsoon months and maximum in the winter months.

(*e*) In all the three electrical elements, the total ranges of variations are very large, and of these, the range of variation of the conductivity is the largest.

(*f*) Considering the mean values of the individual months, the current is maximum in September and is equal to 144×10^{-18} ampere per sq. cm. and is minimum in November and is equal to 20×10^{-18}, ampere per sq. cm. The annual mean value of the current obtained from the values of the several months, is 68×10^{-18} ampere per sq. cm. and the corresponding values of the conductivity and the potential gradient are 137×10^{-18} ohm.$^{-1}$ cm.$^{-1}$, and 65 volts, per metre, respectively.

(3) From the records obtained during abnormal conditions, such as rain, thunder-storms, etc., it is found that :—

(*a*) Drizzle gives sometimes positive, and sometimes negative charge to the test plate.

(*b*) During moderate and heavy rain, not associated with thunderstorm, the test plate is violently charged and the sign of the charge is positive ; the potential gradient is very often reversed and remains negative during most part of the rain.

(*c*) Distant thunder-storms whose occurrences are indicated by lightning flashes and discharge in quick succession, taking place low on the horizons, appear to have no effect either on the earth-air-current or as the potential gradient.

(*d*) During near thunderstorms the potential gradient is reversed and undergoes violent and rapid fluctuations ; and the test plate is violently charged. Also during rainfall from these thunder clouds, the potential gradient undergoes similar charges and the test plate is violently charged, mostly with positive electricity.

AUTHOR.

III.—*An X-ray Investigation of the Crystals of Acenaphthene and Triphenylmethane* : L. A. DESOUZA, Royal Institute of Science.

(1) The Crystal Structure of the crystals of acenaphthene and triphenylmethane have been investigated by the rotation and oscillation method. The dimensions of the unit cell are

Acenaphthene

a_o : b_o : c_o

8·31 Å : 14·07 Å : 7·21 Å°

Triphenylmethane

14·71 Å : 25·71 Å : 7·55 Å

(2) The crystals of acenaphthene belong to the space group Q^5 ,of the orthorhombic bipyramidal class and there are four molecules per unit cell. The crystals of triphenylmethane belong to the space group C_2v^9 of the orthorhombic pyramidal class and have eight molecules in the unit cell.

(3) Calculation of structure factors in the case of acenaphthene crystal show that the molecular orientations suggested by Krishnan from his magnetic measurements do not satisfactorily explain the observed X-ray intensities. The results have been discussed.

AUTHOR

IV.—*The Convection and Variation of Temperature near a hot surface*: M. K. PARANJPE, India Meteorological Department, Poona.

Part I.: The paper discusses the formation of the dark or dust-free layer in the space between a hot surface (above) and a cold surface (below). The variations of the dark layer (1) with distance between the surfaces when the temperatures of the two surfaces are kept unaltered and (2) with the temperature gradient when the distance is kept constant at 3·5 mm. have been studied. It is shown that when the distance between the two surfaces is less than 4 mm. the whole space is occupied by dark layer. If smoke is introduced into this space it travels from the hot to the cold surface with a velocity proportional to the temperature gradient. The excess of pressure associated with the velocity of the particle is calculated. The investigations are continued at different pressures and with particles of different sizes. The applications of interferometry to the study of the phenomena near a hot surface will be discussed in the next part of this series.

Part II.: The paper describes an interferometric method of measuring temperature distribution near hot surfaces. The details of the method and the various precautions to be taken are discussed. The distribution of temperature in the case of a horizontal air cell between a hot surface above and a cold surface below is discussed in relation to convection and the importance of using small air gaps (2 mm. or less) in thermal conductivity measurements is pointed out. Pictures of interference pattern when the air cell is 1·61 mm. and 0·77 mm. thick are given along with the temperature distributions calculated from these pictures.

AUTHOR.

V.—*The Study of Oxy-Coal Gas Flame By Band Spectra*: By J. M. PATEL, Royal Institute of Science, Bombay.

(1) Gross intensities of C_2 (swan) system excited in oxy-coal gas flame with varying mixtures of coal-gas and oxygen have been measured by the method of photographic photometry, using a standard lamp and a calibrated step-slit.

(2) The methods and technique of spectral photometry both general and as applied to band intensities are treated in detail.

(3) The transition probabilities derived from the potential energy curves using Morse's and *Rydbeg's* expressions have been given and compared with the experimental results.

(4) The effective temperatures are derived on the assumption of the statistical equilibrium of molecule in different vibrational levels in the case of all the five gas-oxygen ratios according to the laws of Maxwell and Boltzmann. The intensity centres have been calculated.

(5) All results, viz., intensities, transition probabilities, temperatures and intensity centres have been discussed in detail and conclusions drawn.

AUTHOR.

VI.—*The Dielectric Properties of some Organic Substance*: D. J. DAVAR, Royal Institute of Science, Bombay.

The density, the refractive index and the dielectric constant are determined at room temperature (30°C & 29°C) for solutions of Oleic acid, Linoleic acid, triolein, Triricinolein and Tristearin in Benzene. The dielectric constant is determined at 7,500 K.C. (40 metres) using the method of resonance and a valve voltameter. The refractive index is determined for Na-lines. The polarizations and the electric moment of the substance are calculated from the Debye equations using the method of least squares. Correction for the effect of the solvent is indicated but not applied.

The electric moment is explained from the point of view of the chemical constitution and structure of the substance. The values obtained are Oleic Acid 1·009, Linoleic Acid 1·208, Triolein 3·158, Triricinolein 4·117 and Tristearin 2·844.

AUTHOR.

VII.—*Intensity Distribution in the Molecular spectra of* ALO *and* CN *systems*. By S. A. *and* N. R. TAWDE, Royal Institute of Science, Bombay.

Quantitative intensity measurements in the bands of Alo $(B^{2}\varepsilon \rightarrow X^{2}\varepsilon)$ system have been carried out using methods of photographic photometry. Various factors of importance in the technique of the work have been noted and duly accounted for. The Alo bands were excited in the carbon arc along with the CN bands (violet), and photographed simultaneously. The peak intensities near the heads of unresolved bands are calculated from these after due correction. These values have been used to derive $\frac{1}{4}$ values and transitions. Following the graphical method of Condon, and using the Morse's and Ryberg's expression for the potential energy functions, theoretical values of maximum transitions have been derived. A comparison between experimental and theoretical values has been made, and points of agreement and departure noted and discussed. "Effective temperature" have been obtained for the zones on the assumption of Maxwell-Boltzmann Distribution within the vibrational levels. All these results have been discussed in the light of the existing theories and conclusions drawn wherever possible.

AUTHOR

VIII.—*Influence of Argon on the Emission of Swan Bands.* By D. D. DESAI, Royal Institute of Science, Bombay.

It has been known that an admixture of the inactive gas with substances emitting spectra results in certain cases in profound modification of these spectra. The Swan system of bands due to carbon molecule is thus produced under the influence of high pressure argon in a discharge tube. The nature of this influence is not exactly known. With a view to study the role of argon in the emission of Swan bands, quantitative study of the intensity distribution in this system under five different pressures of argon, viz., 10, 15, 20, 25, 30 mms. has been undertaken. Methods of photographic photometry involving the use of calibrated standard lamp in conjunction with a step-slit of seven different apertures have been used. Intensities have been read from microphotometer records and expressed on a relative scale after due corrections.

The results have been utilized to discuss the following points:

(1) The critical pressure of argon for the production of Swan bands.

(2) The transition probabilities and the potential energy functions due to Morse and Rydberg.

(3) The energy changes in the discharge tube resulting in the production of Swan system.

(4) The statistical weights and intensity shifts with argon pressure.

(5) The effective temperatures on the basis of Max-well-Boltzmann distribution of vibrational energy.

N. R. T.

IX.—*Studies in Hygrometry.* By D. S. LUKTUKE, India Meteorological Department, Poona.

An optical hair hygrometer has been designed and used to study the behaviour of hair as an indicator of humidity in upper air instruments. Experiments were carried out with the ordinary hair hygrograph

(*a*) at room temperature,
and (*b*) at low temperatures in cold storage rooms.

Also experiments were performed on single fibres of hair and other materials like horse hair, cocoanut fibre, paper cellophane, etc. The theory of hair-hygrometer with special attention to the present views of the structure of hair is discussed. The hair hygrometer is used to study the variation of humidity near an evaporating water surface.

K. R.

X—Abstract of the thesis submitted by Mr. N. L. Phalnikar for the M.Sc. degree of the Bombay University, October 1936. M. R. Science Institute, Gujarat College, Ahmedabad.

Part I—*Influence of α-phenyl group in Three Carbon Tautomerism.* II.—*Synthesis and Derivatives of ββ diphenyl glutaric acid.* III—*Chemical investigation of the seeds of Hygrophyla Spinosa.*

Part I—(a), (b), (c).

The influence of various alkyl substituents in different positions on the mobility and equilibrium in the Three Carbon System of the type.

Where R_1, R_2, R_3, R_4 are alkyl groups or portions of alicyclic rings and X is a negative group of the type—$COCH_3$,-$COOC_2H_5$,-CN,-COOH, has been extensively studied by Kon Linstead and their collaborators. In the present thesis the influence of α-phenyl group on the mobility and equilibrium of such a system is investigated. The following pairs of acids and esters were prepared in a pure condition.

α-Phenyl cyclohexenyl acetic acid ; α-Phenyl cyclohexylidene acetic acid.

α - Phenyl - Δ^aHexenoic acid ; α-Phenyl-Δ^b hexenoic acid.

Ethyl α-Phenyl cyclohexenyl Acetate ; Ethyl- α-phenyl cyclohexylidene acetate.

Ethyl α-phenyl-Δ^a hexenoate ; Ethyl α-phenyl-Δ^b hexenoate.

The tautomerism of these, under the standard conditions of Linstead (*J. C. S.*, 1927, 2581) and Linstead and Kon, (*J. C. S.*, 1929, 1269), using the idometric method of Linstead and May (*J. C. S.*, 1927, 2565), for the estimation of $\alpha\beta$ and $\beta\tau$ unsaturated compounds in a mixture, has been investigated. The following table summarises the results :

TABLE

Compounds.	Catalyst used.	% of $\alpha\beta$ at Equilibrium.	mobility.
α-Phenyl cyclothexenyl acetic acid.. α-Phenyl cyclohexalidene acetic acid	KOH	42.	0·00954
α-Phenyl Δ^a hexenoic acid .. α-Phenyl Δ^b hexenoic acid ..	"	87.	0·4854
Ethyl α-phenyl cyclohexenyl acetate .. .. Ethyl α-phenyl cyclohexylidene acetate	Naoet	72.	0·996
Ethyl α-phenyl Δ^a hexenoate .. Ethyl α-phenyl Δ^b hexenoate ..	"	95.	35·65

The results, when compared with those of the corresponding unsubstituted and the α-methyl compounds, show that the phenyl group influences the mobility and equilibrium by its steric and conjugative effects.

I(C) Synthesis and constitution of α-phenyl glutaconic acid.

A glutaconic system differs from a three carbon system of the above type in having an activating group at both ends of the system. Hence it was thought desirable to synthesise and study the properties of α-phenyl glutaconic acid. The existing methods for the synthesis of glutaconic acids being inapplicable for the preparation of α-phenyl glutaconic acid a new method had to be devised which is as follows :—

An ester having a CH_2 group next to a carboxyl group can be condensed with ethyl formate in presence of molecular sodium or sodium ethoxide, to give a mixture of an aldehydic ester and a hydroxy methylene ester. The aldehydic ester is then condensed with malonic acid in presence of pyridine and piperidine yielding the acid ester of the glutaconic acid which on hydrolysis gives the glutaconic acid.

α-Phenyl glutaconic acid has been synthesised and its constitution has been proved to be trans αβ.

Various derivatives, such as, hydroxy anhydride m.p. 175-76°, chloroanhydride m.p. 110-111°, trans [illegible]ianilide m.p. 96°, cis semi anilide m.p. 156°, and dianilide m.p. 90° have been prepared.

Methylation of α-phenyl glutaconic has been tried and it has been shown that the methylation occurs at α-carbon atom.

Part II.

As substituted phenyl glutaric acids were required in this laboratory for the study of the influence of phenyl group on the carbon valency angle, synthesis of hitherto unknown ββ-diphenyl glutaric acid has been effected.

Scheme for the synthesis is as follows :—

Benzophenone dichloride is condensed with ethyl sodio malonate under pressure giving ββ Ethyl diphenyl propane αααα, tetra carboxylate, which on hydrolysis and decarboxylation gives ββ diphenyl glutaric acid m.p. 162-63°.

Many derivatives such as Diethyl ester b.p. 235° at 7 m.m. dimethyl ester b.p. 210° at 30 m.m., diamide m.p. 172°, dianilide m.p. 185°, and imide m.p. 188°, have been prepared.

Part III.

The seeds of hygrophyla spinosa have been subjected to a systematic chemical analysis. No alkaloid was detected. A fixed oil was obtained in 21% yield. Physical and chemical constants of the oil have been determined.

The solid acids contain myristic acid 5·5%, palmitic acid 73% and stearic acid 21·4%. The liquid acids contain linolic, oleic acid and probably an acid of higher molecular wt.

N. L. P.

XI—Abstract of the thesis of Mr. N. K. Joshi, submitted to the University of Bombay for the M.Sc. degree. Wilson College, Bombay.

"*Application of the Phase rule to Binary and Ternary systems.*"

The following Binary systems : (1) Zinc sulphate and water, (2) Magnesium sulphate and water, (3) Manganese chloride and water, and Ternary systems : (1) Zinc sulphate, sulphuric acid and water ; (2) Magnesium sulphate, sulphuric acid and water ; (3) Zinc sulphate, magnesium sulphate and water ; (4) Manganese chloride, hydrochloric acid and water ; (5) Urea, sodium chloride and water were studied.

In all these cases, N. Campbell's bottle was used for attaining the equilibrium of the system and for filtering solution from the solid with which it was in equilibrium. In each case the composition of the solid and the solution was determined.

In the study of Binary systems, the composition of solution and of solid residue at various temperatures gives the solubility of salt, the number of hydrates that can be formed and the transition temperatures of these hydrates.

In Ternary systems containing sulphuric acid, it was found that the solubility of salt decreases with increasing amounts of sulphuric acid. The various hydrates which are formed and remain stable at higher temperatures only, are found to be stable at room temperature, in presence of different amounts of sulphuric acid.

In the case of Ternary systems containing hydrochloric acid, the solubility of the salt decreases with increasing amounts of hydrochloric acid, but the hydrate stable at a high temperature could not be obtained at room temperature by adding any amount of hydrochloric acid.

In the study of Ternary systems : (1) Zinc sulphate, magnesium sulphate and water, and (2) Urea, sodium chloride and water, no double salts could be detected. Formation of mixed crystals may be possible.

S. C. D.

NOTES AND NEWS

A perusal of the addresses given by the Presidents of the British Association during recent years at the annual meetings reveals their anxiety as to the way in which society reacts to the discoveries of science. The question which is agitating the minds of a large number of scientists at the present day is the relationship between science and society. There is a group of persons who think that scientists should carry on their work without concerning themselves as to how their researches would affect the society. They disclaim any responsibility resulting from their discoveries and their publication, or for the use or misuse made of those discoveries by others. There is another group of persons, which is large and increasing, who hold a different view and say that a scientist is also a member of society and a citizen of the state and as such has his duties and responsibilities to them both. The point which has been brought out in this discussion is that too much attention has hitherto been given to researches in the science of matter and too little in the science of man. This brings about a lop-sided development of human nature and is supposed to be one of the causes of the present menace to society. This brings us once again to the age-old question of "Man, Know Thyself". The importance of the study of man was recognized in the olden times, lost sight of in the middle ages, and partially recognized once again with the study of the biological sciences in the latter part of the nineteenth century, but its full significance has been brought home only lately in the light of recent world events, the impending crisis and threat to modern civilization.

Various proposals have been put forward to remedy this state of affairs, for example, the proposal for the formation of a "Chamber of Science" by Sir Gowland Hopkins and a "Scientific League of Nations" by Ritchie Calder. These suggestions have been made with a view to socialize science and avert the danger to society consequent upon the misuse of the forces of nature which man is now able to control. Progress in man's moral nature has not kept pace with his intellectual progress. To restore equilibrium between the development of the head and that of the heart there was a proposal to close down research laboratories for some years. There was also a proposal to do away with the use of power and scrap machinery as they were displacing labour and producing unemployment. Had these suggestions been followed it would have set back by many years the hands of the clock of progress. Our view is that we should have research laboratories and more of them; we should have more machines and labour-saving devices and greater use of power to do the routine work so as to save man from drudgery and soul-destroying work and give him more leisure to devote to higher pursuits in life and bring out the finer qualities latent in him. Let us make a greater and greater use of the scientific method not only in scientific researches but in all branches of knowledge and all departments of life, at home and in society. Let us have all these for they are indispensable, but will that solve the question which is confronting us?

Our interpretation of the situation is that the phase through which science is passing now is necessary and inevitable, though transitional. The discussion in which a large number of scientists, many of whom Fellows of the Royal Society, took part in the columns of *Nature** on the advisability or otherwise of the use of metaphysics in scientific research—which is a new departure in the strictly scientific method of investigation—lends support to the same view. With the evolution in the phase of the consciousness of man from the stage of the concrete mind to that of the abstract and then to that of the intuitional, the evolution in the method of research from that of inductive to metaphysical and then to occult is bound to take place. The crisis through which the world is passing, the great upheavals we see in all departments of life, is due to the human consciousness beginning to unfold the earlier stages of its next phase, namely the intuitional whose characteristic is unification, as opposed to that of the intellectual whose characteristic is separation, isolation. We have already seen this transition accomplished by the radio, the wireless, the aeroplane, which have unified the distant parts of the world as nothing else could have done. The world is indebted to the scientist for this great achievement. But this is a mere superficial union inasmuch as the world is not yet free from threat of another great war which, if precipitated, would destroy our glorious western civilization. There is, however, no real union of head and heart in the statesmen and peoples of different nations. We do not yet feel that we are all parts of one organism; we have not yet reached the stage when we would feel that whatever our interests, our race, our colour, our creed, we are all brothers and that we rise and fall together. This stage will be reached only by right knowledge and understanding of what man really is and how he is constituted, by knowledge of his How, Whence and Whither, of his purpose in life, of his goal and destiny. The present menace to society and threat to civilization have drawn the pointed attention of all interested in the solution of the problems confronting the world once again to the study of man.

**Nature*, 8-5-37 and 12-6-37.

Man has conquered the external world but has yet to gain conquest of his inner nature. It is this orientation, this change of outlook, this inner change, which is required more than anything else to solve the knotty problems facing humanity at present. We are of the opinion that this change of vision in one's outlook cannot be brought about by the study of man from without by the orthodox scientific method. An altogether different method of study is required, a study of the man from within by himself which involves at the same time the undergoing of a certain discipline. Tuition has to be supplemented by in-tuition, sight by in-sight. This discipline inculcates the highest morality, the living of a most unselfish life, a life of spontaneous service and sacrifice. This particular training and discipline is just as necessary for the study of man from within and developing the latent faculties in him as the hard training which a scientist has to undergo for the study of man from without by the ordinary scientific method of research. Such a man, though he becomes aware of and develops the powers latent in him—powers of which orthodox science has no knowledge and which are greater than the forces of nature which science is now able to control—will not be a menace to society, for he will use these powers only for the good of humanity. This shows the rationale for a study of the *whole* man, from without by the ordinary scientific method, from within by the occult method. Such a study in our opinion will go a long way in bringing about a new orientation of thought, which is so very badly needed at the present day to solve the many complicated problems facing society. Every man and woman is a potential occultist. And the scientist of to-day is the occultist of to-morrow.

D. D. K.

REVIEWS

Physics. An Introductory Text-Book : By PROFESSOR H.J. TAYLOR, Wilson College, Bombay. (Published by Humphrey Milford, Oxford University Press). 1937.

Among some of the publications that have recently come out to meet the requirements of the Bifurcation course in Physics of the Bombay University, is the present book by Professor Taylor. It is proper that a book such as this should come through the pen of one who has been teaching and examining the subject in this University for some years now and is in a position to know the defects and shortcomings of our students.

The subject-matter of the book is divided into 18 chapters distributed in 5 branches of Physics viz. general physics and properties of matter, sound, heat, light, electricity and magnetism. The concluding chapter indicates the direction in which the physics of present day is developing. This is followed by a few select examples meant for testing the theoretical knowledge and principles gained through the previous pages. A welcome feature of the book is to lay stress and expand explanation on those abstruse points which generally remain unintelligible to many a student. For instance, the author could successfully dilate on such points as the distinction between mass and weight ; the interference of sound vibrations to form stationary waves ; the light as a form of energy ; the resemblance of electrical dipole with a magnet and the magnetic poles in relation to electric charges. But at some places such expositions appear to be too artificial and confusing. Thus the author in attempting to show the distinction between relative density and specific gravity has defined the latter as the force per unit volume and as such, it is to be expressed in units of force having dimensions of $(M)\ (L)^{-2}\ (T)^{-2}$.

This is certainly not the same thing as denoting it by the ratio between the weight of a body and the weight of an equal volume of water which is the generally accepted notion. Such a definition is entirely misleading and will not go a long way without causing a good deal of confusion.

It has, however, to be seen whether the book really satisfies the requirements of both the new first year and Inter Science courses in Physics. The author in his aim for conciseness consistent with clarity has either left out or insufficiently treated many portions which can be said to be essential in a book meant for elementary students. Even though it may be admitted that the reading of a text-book is accompanied by a course of lectures, in an elementary class it is always necessary for a lecturer to expound fundamental principles before going over any corollaries or applications. The ideas which a beginner finds difficult to grasp by reading a book can be well impressed upon him during the course of a lecture. The teacher therefore has to find time to cover not only the text-book but to supplement what according to author the text-book should not usurp. In practice, the teacher's time is limited and hence he may not be able to do justice to the entire curriculum. We may point out some omissions below. They might serve as suggestions for the second edition.

In the elementary portions, the specific purpose of each of the devices for measuring length should have been briefly stated. The theory of balance should by preference be included in a text-book of theoretical physics. This is not at all given. It should have come immediately after the principle of levers. Only a passing mention of balance is made on p. 9 which is not enough. Matter pertaining to coefficient of friction on pp. 115-116 could very well have been included in Chapter III. We should have expected at least the mention of Cathetometer in Chapter I, the different types of pressure gauges in Chapter V and the property of porosity of matter in Chapter VI. It is not possible to refer in detail to other minor omissions.

Considering the scope of the first paper of I.Sc. course, which includes besides sound, the advanced portions on heat and light, it is difficult to understand why no reference has been made to the instruments for measuring radiant heat. There is serious omission of a coherent account of kinetic theory of gases including Graham's law, Henry's law, Dalton's law and viscosity measurements. Detached references to kinetic theory such as those on pp. 86-87, for the explanation of gas pressure, and Brownian motion and diffusion in Chapter VI could well have been comprised together to form an independent chapter on Kinetic theory. The treatment of polarisation on p. 294 is inadequate considering that it is an idea introduced in the book for the first time. No mention is to be found to ultra-microscope though it is specifically mentioned in the University curriculum.

As the scope of the second paper in Physics is confined entirely to current electricity, we should expect more exhaustive treatment of this subject in the book. Some of the portions, however, require to be greatly supplemented by sections on thermo-electricity and the applications of the thermopile, the measurement of radio activity, Roentgen rays and the electric power installation and distribution.

Some mistakes appear to have crept in. Formula for the frequency of a vibrating stretched string on p. 122 has been derived to be $n = \frac{2}{L}\frac{\sqrt{F}}{P}$ instead of the usual formula $n = \frac{1}{2L}\sqrt{\text{[illegible]}}$. This is likely to create some confusion. Similarly on p. 338, there appears to be printers' mistakes. Instead of $\frac{q}{r_2}$ there ought to be $\frac{q}{r^2}$ in the formula for the difference of potential.

A new convention of signs on the basis of the Physical Society's Report on Geometrical Optics (1934) has been followed in the book, which leads to identical formulas for mirrors and lenses. Such a convention, though simple and convenient, is likely to cause confusion so long as it is not universally adopted by teachers and authors. As a new departure, it could have been added as an alternative to the current one.

It would thus appear that the book is not likely to serve as a comprehensive treatise for the purpose for which it was designed. With some exceptions, it can be said to be more than sufficient for the First Year Science Course but would fall short of I.Sc requirements. Its value, however, as a book of general reading in the subject is beyond question and it can very well be read along with other treatises on the theoretical and the practical.

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EXCHANGES

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† Chief, Periodical Division, United States Dept. of Agriculture Library, Washington, U. S. A.

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* Only Nos. 2 and 4 (for the purpose of abstracts).

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The Dean, College of Agriculture, Laguna P. I., University of the Philippines, Philippine Islands.

Department of Agriculture and Commerce, Scientific Library Division, Manilla, Phillipine Islands.

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Director, Institute of Educational Research, Sun Yatsen University, Canton, China.

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* The Librarian, Cotton Research Station, Trinidad, B. W. I.

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† General Editor, Indian Science Abstracts, 1, Park Street, Calcutta.

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‡ Librarian and Editor, The Academy of Natural Sciences of Philadelphia, Nineteenth and the Parkway, Philadelphia, U.S.A.

Librarian, Division of Plant Industry, 590, Vermeulen Street, Pretoria, Transvaal.

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Librarian, the Rice Institute, Houston, Texas, U.S.A.

Librarian, Smithsonian Institution; Washington, U.S.A.

‡ Managing Editor, *Indian Journal of Venereal Diseases,* 94-97, Girgaum Road, Bombay 4.

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Secretary General, Institute Italiano per 11 Medio Ed. Estremo Oriente, Roma.

Secretary, Scientific Advisory Board, Indian Research Fund Association, Simla.

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Taihoku Imperial University Library, Taiwan, Japan.

The Chief, Scientific Library Division, P. O. Box 774, Manilla P. I.

The Curator, Oriental Mss. Publication Department, Trivandrum (Travancore).

The Director of the Psychological Institute, Sendai, Japan.

The Director, Industrial Research Bureau, Imperial Secretariat Buildings, North Block, 2nd floor, New Delhi.

* The Editor, Biological Abstracts, University of Pennsylvania, Philadelphia, U. S. A.

The Editor, *Thought,* a quarterly of the Science and letters, 329W, 108th Street, New York, U. S. A.

The Field Museum of Natural History, Roosevelt Road, and Lake Michigan, Chicago.

The Hon. Secretary, Tanjore Maharaja Sarfoji's Saraswati Mahal Library Committee, Tanjore.

The Librarian, General Library, British Museum (Natural History) Cromwell Road, London S. W. 7.

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ARTICLES CONTENTS

SOME ASPECTS OF THE SURFACE TENSION AND OSMOTIC PRESSURE OF NORMAL URINE .. .. S. N. NARAYANARAO 1
BACTERIAL LEAF-SPOT OF SOYBEAN IN BOMBAY .. . .. . B. N. UPPAL, M. K. PATEL & M. N. KAMAT 16
A STUDY OF THE EFFECT OF AMIDO-PYRINE ON THE BLOOD MORPHOLOGY & LEUCOCYTOGENESIS IN RATS . .. . A. S. PARANJPE & S. V. KANITKAR 19
STUDIES IN FŒTAL STOMACH AND APPENDIX .. R. C. MOTWANI 27
MEASUREMENT OF INDIAN PELVES .. . Dr. P. S. DASTUR 31
THE VIABILITY OF CERTAIN PATHOGENIC MICRO-ORGANISMS IN VARIOUS FRESH FRUITS OF INDIA .. F. R. BHARUCHA & K. H. BHARUCHA 35
A NOTE ON SOME ABNORMALITIES IN PLANTS COLLECTED IN BOMBAY—II R. E. COOPER & ELLA GONZALVES 41
BULBILS OF REMUSATIA VIVIPARA SCHOTT .. . . T. S. MAHABALE & G. S. DESHPANDE 47
PHYLLODY IN THE FLOWERS OF CROTALARIA STRIATA, DC. .. R. E. COOPER 57
STUDIES ON THE VASCULAR CRYPTOGAMS OF THE BOMBAY PRESIDENCY —PART I .. .. T. S. MAHABALE 62
THE SKELETON OF PERIOPHTHALMUS BARBARUS (LINN.) . .. . Dr. S. H. LELE & R. D. KULKARNI 76
A SHORT NOTE ON THE CILIATED APPARATUS IN THE ECHIURUS LARVA P. R. AWATI 92
STUDIES IN THE VASCULAR CRYPTOGAMS OF THE BOMBAY PRESIDENCY —PART II .. .. T. S. MAHABALE 104
DEVELOPMENT OF THE FEMALE PROTHALLIUM IN AZOLLA PINNATA, R. BROWN .. .. B. N. MULAY 118
LIST OF THESES FOR M.Sc. DEGREE 125
REVIEWS 126
BOOKS RECEIVED 128
ACKNOWLEDGMENTS 129
EXCHANGES 131

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VOL. VI MARCH 1938 PART V

SOME ASPECTS OF THE SURFACE TENSION AND OSMOTIC PRESSURE OF NORMAL URINE

(*With 5 graphs and 7 tables*)

By

S. N. NARAYANA RAO, M.Sc.

(*Department of Physiology, Seth Gordhandas Sunderdas Medical College, Parel, Bombay.*)

A study of the physical characteristics of the body fluids is being made for some time past and has been one of great promise. It is proposed to communicate in this paper the results of investigation on normal urine in regard to Surface tension and Osmotic pressure. This body fluid being a complex colloidal excretion has yielded results of importance, and further study of the other physical properties and equilibrium conditions of this fluid and other body fluids is bound to yield results of great value.

All the specimens of urine for investigation were collected from the students of the College. By limiting the choice of collection to healthy medical students normal urine could be secured in abundance. The study having been in the first instance confined to normal urines of healthy individuals it was necessary to have a large variety of the specimens.

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Before a detailed examination of its physical properties, the specimen of urine was thoroughly examined in order to be sure that it was normal. For this purpose the usual routine chemical tests were made. All those samples which were suspected to contain any of the abnormal constituents were rejected.

Surface Tension.

The physiological variations in the Surface tension of urine have been studied, although very briefly by Duhot and Gernez[1] employing a stalagmometer. A more comprehensive study has been made recently by Perryman and Selous.[2] The latter have made use of the method developed by Jaeger. The other two common methods, viz. the tensiometric method which has been recently perfected by Du Nouy,[3] and the capillary height method have not been favoured by them.

The present investigations were, however, undertaken with a stalagmometer. The results show that they are as reliable as those obtained by Perryman and Selous and in point of speed this instrument is quite as good. Some of the observations agree with the findings of the above authors and this fact will be referred to later on.

The theory behind this method is quite simple and has been extensively studied. The surface tension, T, is obtained from the formula

$$2\pi rT = W = v. d.$$

where $2 \pi r$ = external circumference of the end of the tube.

v = Volume of the drop

d = Its Specific gravity.

The simple formula given above is only an approximation. It has been shown by Lohnstein,[4] Harkins and Brown[5] that a more accurate formula is given by the expression

$W = mg = 2\pi\, r. T. \phi$ where ϕ is a correction factor dependent on the ratio of the radius of the tip, r, to the linear dimensions of the drop as expressed by the cube root of its volume. The value of the correction ϕ is practically constant when $r/v^{\frac{1}{3}}$ lies between 0·76 and 0·95. In the present investigation this factor has been taken into account. In order that the same area of surface be wetted each time, the end of the tube is ground off at right angles to its length and polished.

The average volume of a drop is obtained by measuring the total volume of a known number of drops and dividing by the number of drops formed. In allowing the drops to form, one important factor has to be taken into account, and that is, the rate of formation or the age of the drop. This factor becomes all the more important in the case of aqueous solutions having surface tension lower than that of water, and complex colloidal liquids like urine; for it takes time for the solute and suspended particles to come to the surface. A different result is obtained when the drops follow in quick succession from that obtained when they follow more slowly. But this aging goes on for considerable time, perhaps for hours, but the greatest changes occur in the first few seconds. To arrive, therefore, at the correct rate of formation of the drops, preliminary experiments were conducted with pure liquids, because in their case, there is little quantitative evidence of change in Surface tension with time although Schmidt and Steyer[6] have shown indirectly that such a change must occur, the time interval being too short to be ordinarily measured. The time found for these liquids and a few solutions also, was taken as the guide in the rate of formation of drops in the case of urine (10 min. 20 secs.) except when the variations of surface tension with time was the subject of study.

There is another factor to which attention has to be drawn. Namely, the evaporation of the drop during the process of formation. In order to prevent evaporation taking place the end of the Stalagmometer is passed through a stopper which fits into the neck of a small bottle. The bottle contains a little of the liquid under test, which saturates the space with its vapour. By immersing this vessel in a constant temperature bath the Surface tension of the liquid could be measured at any desired temperature.

The values obtained for the surface tension of some liquids during preliminary experiments were as shown below :—

1. Water	... 71·68	dynes/cm. at 20°C	72·7	dynes/cm. (From standard at 20°C tables)
2. Glycerol	... 64·8	„	65·2	„
3. Benzene	... 28·1	„	27·9	„
4. Ethyl alcohol	... 23·5	„	23·3	„

The results show a good agreement with the standard values. In practice the stalagmometer was thoroughly cleaned and dried before each determination. During the course of the work the surface tension for distilled water was determined for verification.

Experimental.

The investigations conducted may be classed as under :—

(1) The variations of Surface tension with time.

(2) Daily variations in Surface tension.

(3) Changes of Surface tension with different individuals.
(4) Relationship between Surface tension and Specific gravity.

(1) *Variation of Surface tension with time.*

In this experiment the time of formation of the drops was varied and its influence on the Surface tension studied. The range of observation extends from 30 Secs. to 20 minutes i.e., from drops formed at the rate of one for every half minute to one for every 20 minutes. The regulation was obtained by connecting the mouth of the stalagmometer with a short rubber tubing and applying a screw type pinch cock to it. By screwing or unscrewing, the speed with which the drops could be had was regulated. The number of specimens examined in this connection was 25.

(2) *Daily variations in Surface tension.*

The object of this enquiry was to find out how the food and drink affect the Surface tension of urine during the course of a day. Samples of urine from ten different individuals were examined. The specimens from each were obtained in the following order :

First morning Specimen passed immediately after rise between	6 & 6-30 a.m.
Second Specimen passed after light tiffin and tea	10-30 a.m.
Third Specimen passed after usual meal.	12-30 p.m.
Fourth Specimen passed after the afternoon tea	2-30 p.m.
Fifth Specimen passed at	5 p.m.

(3) *Changes of Surface tension of normal urine with individuals.*

For the purpose of this study only the first specimens passed in the morning by 40 normal individuals were examined. The surface tension of the morning specimens being the lowest, as observed from daily variations, they were considered most suitable ones for comparison with one another.

RESULTS.

(1) *Surface tension—Time experiments* :—

Tables 1 and 2 show the changes which occur in the values of Surface tension of urine with time. The same have been plotted graphically to illustrate the nature of the change. (Graphs 1 & 2.) The results confirm the observations of Perryman and Selous. There is a similarity in the shape of the curves and there appears to be conclusively a logarithmic relationship between time and Surface tension. The relationship is

$$T = T_0 - K \log. t$$

where K = Constant.

The value of this Constant varies with individuals and remains the same for the same individual. The results lead to the conclusion that the structure of the surface is constantly changing and tending towards equilibrium. By extrapolation of the Surface tension log. t curve, the dynamic value of the Surface tension is found to lie between 68 and 70 dynes/cm.

The characteristic results of daily variations of Surface tension of normal urine for a given individual of three males have been recorded in table 3. Graph 3 shows its graphic representation. In general the Surface tension in the morning is the lowest. This fact has been noticed by several workers. Then there is a steady rise, reaching a maximum by noon, the highest value recorded being 69·8 dynes/cm. Towards the close of the day this again declines. However, these fluctuations are not governed by any mathematical law. Nor are they the same for all subjects.

In regard to the Surface tension of urines of several individuals mentioned in the experimental part there appears to be no agreement at all. Table IV gives 18 of the readings recorded. One point emerges clearly. The minimum value of the Surface tension varies within certain limits, 62 to 69 dynes/cm.

About the Surface tension and specific gravity of normal urines the two do not appear to be correlated. In one set where the fluctuation of specific gravity was between 1·007 and 1·014 the normal distribution of Surface tension value was between 68·74 to 59·82 dynes/cm. In a second set, when the range of change of specific gravity was from 1·016 to 1·023 the surface tension values lay between 68·9 and 54·3 dynes/cm. and so on. Again even when the specific gravity remained the same in some cases, the Surface tension value had altered. There is, therefore, little reason, to attribute any relationship of Surface tension with specific gravity as Schemensky[7] does.

OSMOTIC PRESSURE.

Record will be made in this section of the results of work done on the osmotic pressure of normal urine under different physiological conditions. The results are important as they will throw light on the nature of control of the kidneys in the maintenance of the normal osmotic pressure of blood. This subject received earliest attention dating back to 1897, when Von Koranyi[8] worked on this problem and on the results of his work suggested its application to diagnostic purposes.

METHODS.

Direct determinations of the osmotic pressure are difficult and cannot be undertaken conveniently owing to manipulative difficulties. Among the indirect methods available, the most important are those depending on the determinations of vapour pressure, the boiling point and freezing point of solutions. A very delicate thermocouple method has been recently developed by Prof. A. V. Hill[9] which can be applied to biological liquids to be had in small quantities (less than 1 c. c.) But the apparatus is rather elaborate. The manipulative and other difficulties preclude its use.

The freezing point determinations are performed with greater ease than determinations of vapour pressure. The boiling point method has to be ruled out in the case of physiological fluids. Thus the freezing point method is the most common used in physiological and medical practice.

The theory of this method has been thoroughly studied and the osmotic pressure is obtained from the relationship.

$$P = 12{\cdot}06\Delta - 0{\cdot}021\,\Delta^2$$

Where Δ = Depression in the freezing point of the solvent and P = the osmotic pressure.

Harris and Gortner have published a table giving the values of osmotic pressure for various values of Δ.

In order that the values obtained for osmotic pressure from measurements of depressions of freezing point of a solvent be reliable several precautions have to be observed. The Beckmann apparatus has been constructed taking into account, and eliminating, the common sources of error in measurement. Apart from these, there are others which have to be considered. For example, when the mercury column of the thermometer contracts, on the solution being cooled, it sometimes sticks in places, and therefore the column breaks, and an accurate reading of the freezing point cannot be measured. This can be prevented by tapping the stem of the thermometer frequently. Generally, when the temperature of the solution is lowered, it will reach some degrees below the actual freezing point of the solution before it freezes. In other words super cooling of the solution takes place before freezing occurs. The moment at which freezing of the solution sets in can be observed generally by the behaviour of the mercury column in the thermometer. When super cooling of the solution occurs freezing is accompanied by an expansion of the mercury column and the temperature of the solution rises rapidly until true freezing point is reached. The maximum value so attained should be taken as the freezing point together with a correction factor. This correction to be applied to the freezing point has been calculated by H. C. Jones for every degree of super cooling. This correction is 1/80 of the observed Δ for every degree of super cooling, and it must be subtracted from the value recorded. In practice it was found to be inadvisable to cool the liquid below two degrees of its actual freezing point. Freezing could be initiated at any stage by dropping in, at the right moment, a small crystal of ice or still better a glass bead in the hollow of which water was previously frozen to ice.

EXPERIMENTAL.

Daily variations of osmotic pressure :—

The first class of experiments conducted pertained to a study of the variations in the osmotic pressure of urine during the course of a day. These variations have been suggested by the works of investigators in this line. Samples of urine were collected as in the case of Surface tension measurement dealing with its daily variation in individuals. The hours of collection were as under :

First Specimen collected between	6 & 6-30 a.m.	
Second Specimen collected between	8 & 8-30 a.m.	after tea.
Third Specimen collected between	10 & 10-30 a.m.	after glass of water.
Fourth Specimen collected between	12 & 12-30 p.m.	after lunch.
Fifth Specimen collected between	2 & 2-30 p.m.	tea only.
Sixth Specimen collected at	5 p.m.	

Thus from an individual six specimens were in all collected and examined. The nature of the meal taken was almost the same in the cases examined. The total number examined like this numbered 8.

Fortnightly variations in the osmotic pressure of urine.

With a view to finding out whether there was any periodic variation in the osmotic pressure of urine morning specimens from the same individual for a fortnight were collected and examined.

Five individuals were selected for this purpose. As the results did not bring to light any regular or periodic or characteristic variations only a small number of cases was examined. The characteristic curve obtained for an individual has been shown in Graph (4), Table (6).

Osmotic pressure of urine for different individuals.

The specimens of urines examined in this connection were obtained after the usual meal of the subjects usually at 12 noon. The number of subjects examined was sixty-five, and the results of 18 are recorded in Table (7).

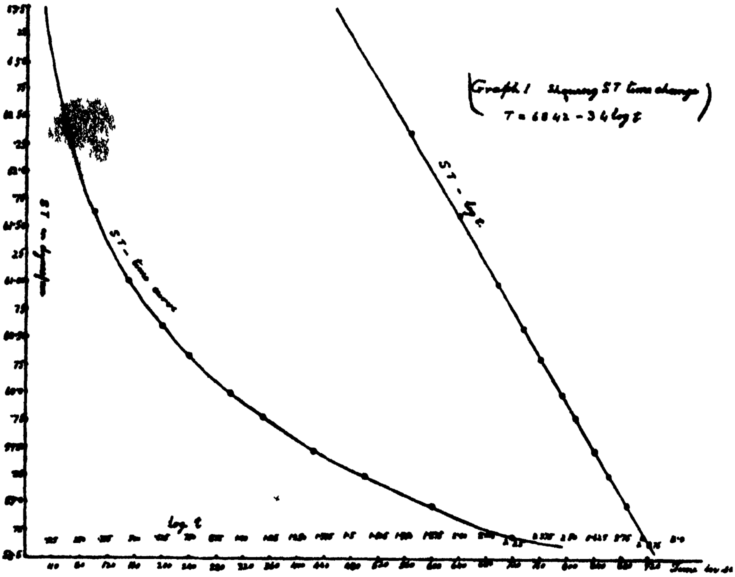
RESULTS.

The results of examination on the changes in osmotic pressure of normal urine show that there is no definite law of variation. As shown by the Graph (5) the variation in △ occurs between wide limits ; 0·8 to 1·8°, 1·2 to 1·6° and so on. The graph also reveals the fact that the concentration of the urine is maximum at noon and therefore depression in freezing point is greatest. Towards the close of the day the osmotic pressure of urine diminishes. These large variations show that the kidneys function in such a manner, throwing out more or less concentrated urine according to the contents of blood, that the osmotic pressure of the latter is kept fairly uniform.

Graph (5) also shows that the daily changes of osmotic pressure vary in different individuals having more or less the same diet and conditions of living.

TABLE I—SHOWING CHANGES IN SURFACE TENSION OF URINE WITH TIME.

No.	Time in seconds	log.t	Tension in dynes per cm.	No.	Time in seconds	log.t	Tension in dynes per cm.
1	30	1·48	63·52	7	300	2·48	59·99
2	60	1·78	62·37	8	350	2·54	59·78
3	10[illegible]	2·0	61·62	9	425	2·63	59·48
4	150	2·18	61·01	10	500	2·70	59·24
5	200	2·30	60·60	11	600	2·78	58·97
6	240	2·38	60·33	12	720	2·86	58·7



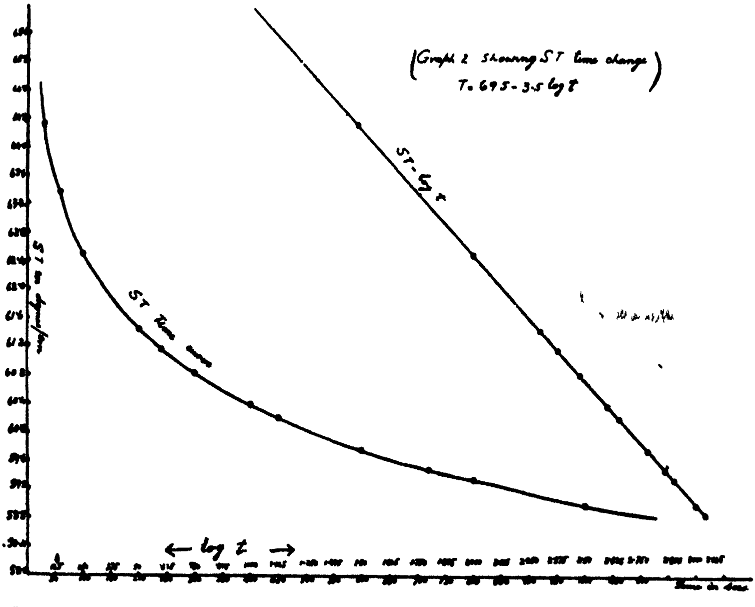
GRAPH 1.—Showing Surface Tension change of urine with time.

TABLE II—SHOWING CHANGES IN SURFACE TENSION OF URINE WITH TIME.

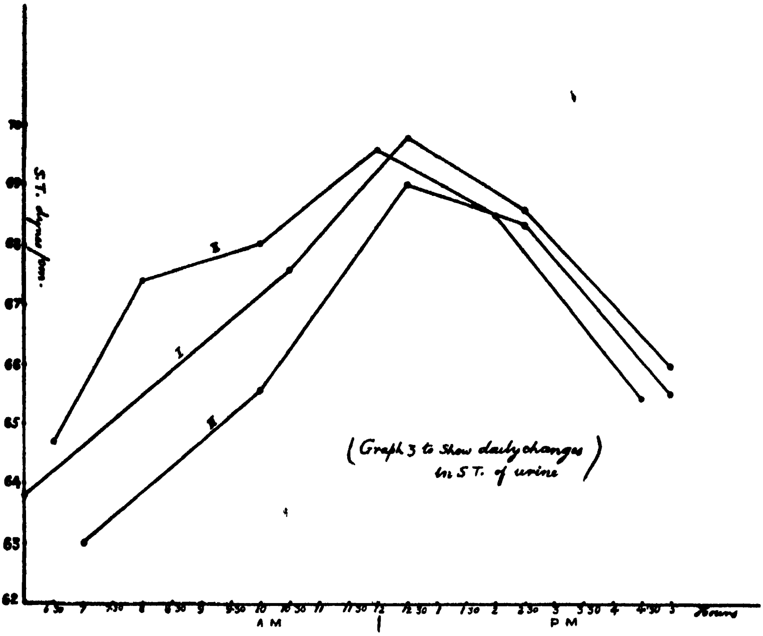
No.	Time in seconds	log.t	Tension in dynes per cm.	No.	Time in seconds	log.t	Tension in dynes per cm.
1	30	1·48	64·32	8	450	2·65	60·22
2	60	1·78	63·27	9	600	2·78	59·77
3	100	2·00	62·5	10	720	2·86	59·49
4	200	2·30	61·45	11	800	2·9	59·35
5	240	2·38	61·17	12	1000	3·0	59·0
6	300	2·48	60·82	13	1100	3·04	58·86
7	400	2·6	60·40				

TABLE III—SHOWING CHANGES IN SURFACE TENSION OF URINE DURING THE COURSE OF THE DAY.

No.	Hours	S. T. in dynes per cm.		
		Subject		
		I	II	III
I	6.00 A. M.	63·8		
	6.30 A. M.		64·7	
	7.00 A. M.			63·0
II	8.00 A. M.		67·4	
	10.00 A. M.		68·0	65·60
	10.30 A. M.	67·58		
III	12.00 Noon		69·61	
	12.30 P. M.	69·8		69·02
	2.00 P. M.		69·0	
IV	2.30 P. M.	68·6		68·35
	4.30 P. M.		65·43	
V	5.00 P. M.	66·0		65·52



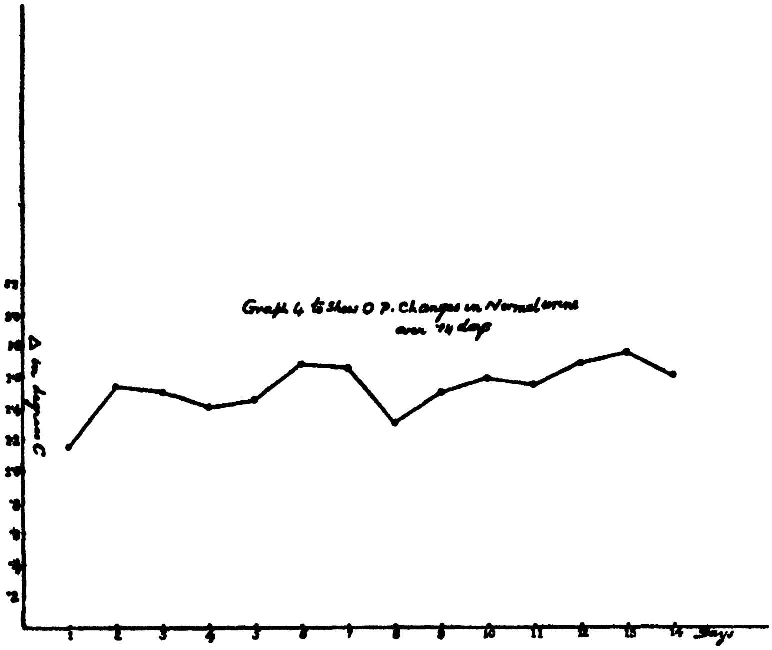
Graph 2.—Showing Surface Tension change of urine with time.



GRAPH 3.—Showing daily changes in Surface Tension of Urine.

TABLE IV—SHOWING SURFACE TENSION OF URINE FOR DIFFERENT SUBJECTS.

No.	S. T. dynes per cm.	No.	S. T. dynes per cm.	No.	S. T. dynes per cm.
1	69·84	7	67·65	13	62·31
2	68·62	8	66·0	14	67·45
3	66·34	9	65·45	15	66·83
4	67·72	10	69·32	16	68·29
5	68·54	11	66·74	17	67·70
6	69·42	12	68·41	18	68·32



GRAPH 4.—Showing osmotic pressure changes in Normal Urine over 14 days.

TABLE V—SHOWING DAILY VARIATIONS IN THE OSMOTIC PRESSURE OF URINE.

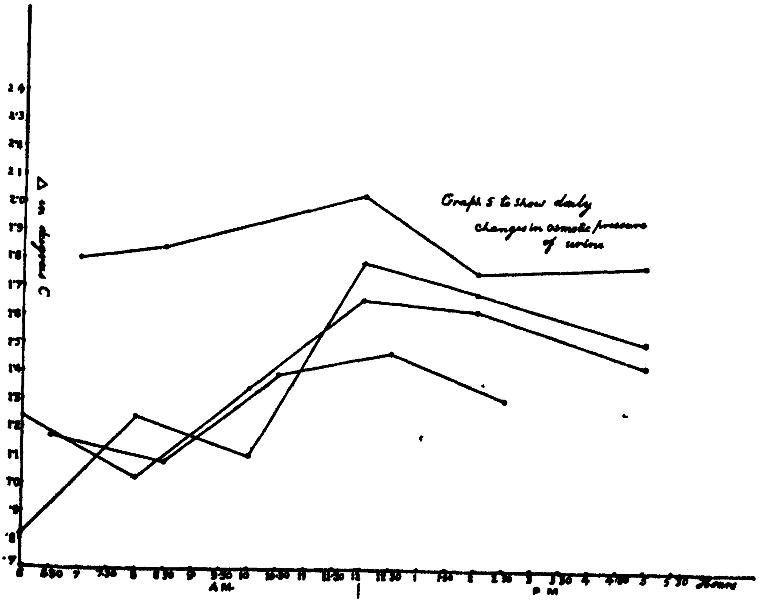
No.	Hour	Depression in Freezing Point in °C.							
		Subject							
		I	II	III	IV	V	VI	VII	VIII
I	6·00 A. M.	0·82			1·24	0·92			0·74
	6·30 A. M.	...	1·17	...	...	...	0·86	0·76	...
	7·00 A. M.	...	...	1·8	...	...	...	...	...
II	8·00 A. M.	1·24	...	...	1·02	1·14	...	...	1·32
	8·30 A. M.	...	10·8	1·84	...	...	1·21	0·94	...
III	10·00 A. M.	1·10	...	...	1·34	0·98	...	...	1·36
	10·30 A. M.	...	1·39	...	...	...	1·17	0·93	...
IV	12·00 Noon	1·79	...	2·03	1·66	1·56	...	...	2·30
	12·30 P. M.	..	1·47	...	...	...	1·48	1·20	...
V	2·00 P. M.	1·68	...	1·75	1·62	1·46	...	...	2·18
	2·30 P. M.	...	1·30	...	...	...	1·44	1·18	...
VI	5·00 P. M.	1·5	...	1·78	1·42	1·38	1·40	1·06	1·71

TABLE VI—TO SHOW THE CHANGES IN OSMOTIC PRESSURE OF NORMAL URINE OVER 14 DAYS.

No. of days	1	2	3	4	5	6	7
Depression in F. P.	1·15°	1·54°	1·50°	1·40°	1·45°	1·68°	1·66°
No. of days	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Depression in F. P.	1·30°	1·50°	1·59°	1·54°	1·68°	1·74°	1·60°

TABLE VII—TO SHOW THE OSMOTIC PRESSURE OF NORMAL URINE FOR DIFFERENT SUBJECTS.

No. of persons	1	2	3	4	5	6	7	8	9
Depression in F. P.	0·82°	1·17°	1·24°	0·92°	0·86°	1·8°	0·76°	0·74°	1·02°
No. of persons	10	11	12	13	14	15	16	17	18
Depression in F. P.	1·14°	0·94°	0·79°	1·05°	0·62°	0·98°	0·94°	1·23°	1·17°



GRAPH 5.—Showing daily changes in osmotic pressure of urine.

SUMMARY AND CONCLUSIONS

The Surface tension and osmotic pressure of normal healthy urine under different conditions both physical and physiological have been studied.

The surface tension has been measured employing a stalagmometer using the more accurate formula.

$W = mg. = 2\pi \, r \, T \, \phi$ where ϕ = constant $r/v^{\frac{1}{3}}$ and it varies between 0·76 and ·95.

For the measurement of osmotic pressure the freezing point method has been employed. And in the determination of Δ allowance has been made for the super cooling of the liquid and the correction suggested by Harry C. Jones has been applied.

That the Surface tension of a sample of normal urine varies with time has been observed. Also there is a definite law of change; for the curves are logarithmic as suggested by Perryman and Selous. The relation is of the form

$$T = T_0 - K \log t$$

where K varies from subject to subject but remains constant for the same subject. Variations in the surface tension of urine during the course of the day on normal subjects show that there is no definite law of variation. But the S. T. of urine of the 1st morning specimen is minimum.

There is little reason to assume any relationship between Surface tension and Sp. gr. of urine, which has been studied. Hence the view of Schemensky cannot be supported.

The osmotic pressure changes of normal urine during the course of a day have been given in terms of Δ, the depression in Freezing Point. There are wide limits of variation, for example, from Δ of 0·8° to that of 1·8° during 12 hours. This shows there is a constant change in the molecular concentrations of solutes and Colloids of urine. The ingestion of food and drink affects the depression in freezing point of urine in such a manner, it seems, as to keep the depression in freezing point of blood uniform.

The fluctuations in Δ of normal urine of a given subject for 14 days have been examined. Although the limits of variations are not wide apart, still the changes are not cyclic. In other words they are irregular.

The author desires to record his indebtedness to Prof. S. P. Niyogi, at whose instance the problem was taken up for investigation and to Dr. Jivraj N. Mehta for the facilities given in the conduct of this inquiry.

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BACTERIAL LEAF-SPOT OF SOYBEAN IN BOMBAY

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Soybean, *Soja max* (L.) Piper, is a crop of recent introduction into this country and is now cultivated on some of the agricultural stations in the Bombay Presidency. A leaf-spot disease was observed in 1934 on the Jalgaon Farm where it was found to be doing considerable damage to the crop. From microscopic examination the disease appeared to be of bacterial origin, and an organism was ultimately brought into pure culture from lesions on leaves. The description of the disease and the results of a study of the morphology and biochemical properties of the organism are briefly described in the following pages.

SYMPTOMS

The lesions on leaves, on first appearance, are minute, chlorotic areas, which slowly turn sanford brown and are slightly raised in the centre. In young spots the raised centres may be seen on both sides of the leaves. These intumescences rupture the epidermis and finally shrivel and slough off. The mature lesions or spots vary in size from minute specks to large brown areas, which latter measure about 2 mm. and are caused by the fusion of smaller lesions. These spots are usually surrounded by yellow borders. Heavily infected leaves prematurely turn yellow and drop off.

The disease is also noticed on petioles and stem where it usually takes the form of long, narrow streaks. Infection of leaf-veins sometimes takes place. Pods have never been found to be infected under natural conditions.

PATHOGENICITY

The organism was repeatedly isolated from lesions on leaves of soybean by the dilution-plate method, and yellow, circular colonies were visible in 4 to 7 days on beef agar and in 3 to 5 days on potato-dextrose agar, at 26-27°C.

In order to test the pathogenicity of the organism isolated from the lesions, soybean seedlings were inoculated with a suspension of the organism by means of an atomizer, and were then kept moist under a bell-jar at 26-27°C. Inoculations were invariably successful, lesions appearing on the leaves in six days. The organism was re-isolated from the lesions. Infection of the following seventeen varieties of soybean was readily achieved : Biloxi, Chiquita, Dunfield, Easy Cook, Haberland, Hahto, Higgan, Illini, Laredo, Mammoth Brown, Mammoth Yellow, Manchu, Mansoy, Ootantan, Peking, Roksum and Virginia.

In order to test the host range of the organism the following leguminous plants were inoculated simultaneously : *Pisum sativum* L., *Lathyrus sativus* L., *Cajanus indicus* Spreng., *Cicer arietinum* L., *Phaseolus mungo* L., *Phaseolus radiatus* L., *Vigna catjang* Walp. and *Medicago sativa* L. The plants were kept moist after inoculation by covering them with a bell-jar. In no case did any of the plants get infected.

The pathogen

The organism is a short rod 0·5 to 0·75 × 1·25 to 2·25 μ ; mostly single but sometimes in chains of two to three ; motile by polar flagella ; without any spores or capsules ; Gram-negative and not acid-fast.

On potato-dextrose agar colonies are small, circular, with entire margins, smooth, slightly raised, pale yellow. Growth in beef bouillon is moderately clouded, with a viscid yellow precipitate, forming a yellow pellicle, exhibiting aerobism. The optimum temperature for growth is 26—30°C. ; no growth at 37°C. Thermal death-point is 48°C. for 10 minutes. The organism liquefies gelatin and has a strong diastatic action on starch (as seen from copious growth on potato cylinders) ; it does not reduce nitrate or produce indol. It makes no growth in Cohn's, Uschinsky's and Meyer's solutions. It reduces litmus milk. No gas is produced in Difco peptone water with the addition of dextrose, glucose, lactose, laevulose, galactose, raffinose, dextrin, mannitol, salicin or glycerol ; whilst acid is produced from dextrose, galactose or glucose. The organism makes good growth on Giltner's congo red agar and absorbs the red from the medium.

It is apparent from the above description that the morphology and biochemical properties and cultural features of the organism isolated from soybean at Jalgaon resemble those of *Phytomonas phaseoli* var. *sojense* Hedges. The symptoms described by Hedges (1924) on soybean are also similar to those observed by us on this host.

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A STUDY OF THE EFFECT OF AMIDOPYRINE ON THE BLOOD MORPHOLOGY & LEUCOCYTOGENESIS IN RATS.*

By

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In 1922, Schultz described a *malady* with the following essential characteristics : Onset nearly always brisk with fever, general malaise, symptoms of toxi-infection, angina with necrotic ulceration of the buccopharynx passing on to gangrene, nearly complete absence of glandular complications or of splenomegaly, diminution in the number of leucocytes, particularly granulocytes which may even completely disappear from the blood, thus showing a deficiency of the bone marrow; but the number of red corpuscles, bloodplatelets, bleeding time and coagulation time remain normal and there is an absence of all hemorrhagic syndromes. The leucogranulocytopoiesia is the only bone-marrow function at fault. Termination is nearly always (in 90%) fatal.[1] In 1930, however, Rutledge and others called attention to benign types of leucopenia with and without mucous membrane lesions and having a tendency to recur.[2] Before Schultz several cases of fatal pharyngitis with leucopenia had been reported but it was he who first described it as a clinical entity and called it *agranulocytosis*. It is now known also by other names like malignant neutropenia, (primary) granulocytopenia,[3] and in 1923 Friedmann called it agranulocytic angina. But the gangrenous lesions are not always localised to the buccopharynx. One may find them in oesophagus, gastrointestinal tract, vulva, vagina or even in the liver. Schultz thought that it was a disease *caused* by a specific microbic agent and some others also took the view that infection was primarily responsible for the failure of the leucocytogenetic function of the bone-marrow, while others that the marrow failure was primary and that the visible lesions were the consequence of the failure of the defensive mechanism, normally

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* The expenses of this work were met from a fund contributed by two of the members of the Honorary staff of the K. E. M. Hospital.

saprophytic bacteria attacking the tissues in a situation where they are always present in abundance.[4] The latter view is supported by the observation that extreme granular leucopenia preceded the appearance of symptoms and lesions. Thus the leucopenia (neutropenia) appears to be the cause and not the result of the bacterial invasion. The correctness of this view is also proved by the later observations.

No one organism has, so far, been found to occur constantly or even more frequently in the clinical lesions. The role of microbic infection is still under discussion, but an analogous blood picture is said to have been experimentally produced in the rabbit with the toxin of streptococcus viridans. Atrophy of the bone-marrow may also result from radiotherapy. There is a predilection of the disease for the female sex and the frequent occurrence of the attacks at the menstrual periods has suggested a possible but entirely hypothetical hormonic dysfunction.[5] However, much of the available evidence points to *intoxication*, either professional or medicamentous. It may be professional, where benzol or its derivatives, bodies eminently toxic to granular leucocytes are used. Kracke has been able to reproduce the clinical picture experimentally in rabbits by the use of benzene and other drugs containing the benzene ring, and he has suggested the etiologic importance of these drugs in the production of this disease. It has also been shown that exposure to benzene of human beings causes, in some, a marked depression of the bone marrow, with especially a marked effect on the granulocytic centres. Well suggested that the incidence of benzene poisoning has been increasing with the increasing use of benzene in industry. Likewise the apparent increase in the incidence of granulocytopenia parallels the increasing use of benzene derivatives and similar drugs. But cases of granulocytopenia have undoubtedly occurred in which no drug has been taken.[6] No explanation is known in such cases. Here the hypothesis of Miller & Rhodes which points to the deficiency of some special dietetic factor may be of practical interest.[4]

Still, the evidence incriminating a certain group of drugs is extremely strong, and they must be considered as etiological agents. *Amidopyrine* is one of them. It is a pyrazolon derivative prepared by Stolz in 1893 and patented in Germany in 1897 under the proprietary name " pyramidon." It is derived from antipyrine and is structurally similar to it. Soon after its preparation, it was used clinically in Germany and has since been in use there as an analgetic, antipyretic, and in recent times for the treatment of acute rheumatism, in place of or in addition to salicylates. But very few cases of agranulocytosis, following its use, have been reported from that country. Dennig[7] studied the effect of amidopyrine treatment in more than 500 cases and followed the blood picture of 50 cases receiving the drug but no case of agranulocytosis occurred in his series, though some patients had exanthems from the use of the drug. Many cases have, however, been reported from America and Scandinavia. In Denmark amidopyrine was not much used till 1925 and agranulocytosis was recognised there in 1934 and now it is there a dreaded disease, as, in the period from 1933 to 1935, there have been 39 deaths from it. It is stated that amidopyrine even when used in, what is considered, a correct dosage has produced more cases of granulocytopenia than any other drug in common use in Medicine. According to Herz,[8] in 1934, 500 cases of agranulocytosis were on record, the increase in the number of cases on record closely paralleling the increase in the use of amidopyrine within recent years. Plum[9] has mentioned 128 cases in which the disease was associated with one or more doses of amidopyrine. The cases recorded in the literature have arisen after doses extending from a single dose to the continued use of the substance for weeks or months. 'The development of agranulocytosis in these cases cannot be merely accidental and that the administration of this remedy has actually caused the disease can be demonstrated only by showing that amidopyrine in therapeutic doses produces granulocytopenia in the patient after his blood picture has returned to normal. This has been done by Plum and other workers, and recently by Holten.[10]

Though these experiments in patients recovered from an attack of the disease show its connection with amidopyrine, the attempts to produce it *experimentally* in animals have not been very successful. Kracke failed to produce it in rabbits by the feeding of amidopyrine. Madison and Squier[11] produced a drop and antemortem disappearance of granulocytes in a rabbit with large doses of allonal (a combination of alurate or allylisopropylbarbituric acid with amidopyrine) but failed in other 17 rabbits. Hoffman, Butt & Hickey[12] obtained some depression in rabbits, but they give no details in their preliminary report. Herz[8] states that his work points to amidopyrine as having a definite effect on the myeloblastic tissue similar in man and in rabbits, but the details of his work are not available. Further, he criticises other workers for having classed barbiturates and amidopyrine among the benzene ring derivatives and point out that the barbiturates contain an incomplete purine ring and not a benzene ring. According to him amidopyrine also should not be called a benzene ring derivative, though there is a phenyl radicle present in its side chain, because pyrazolon is the active element of the drug. He considers the NH component of the ring as the toxic element, regardless of whether it remains as NH or whether H is replaced by another radicle, such as phenyl in antipyrine or amidopyrine.

All these previous experiments have been performed on rabbits. We have attempted to study the effects of amidopyrine on the blood condition *of rats* by the method employed by Smith & Hambourger[18] to study the effects of another antipyretic (acetanilid) on the blood morphology. We gave repeated (daily) doses of amidopyrine for three to four months or longer to ten rats, while five other rats (Nos. 1 to 5) were placed under identical (dietetic and other) conditions to serve as controls. Our observations consisted of determinations of hæmoglobin, erythrocytes, leucocytes including differential counts, reticulocytes in their blood at frequent intervals. A record of their weight was also kept as it is an indication of the well-being of the animals.

EXPERIMENTAL

Young adult animals, males and females, were used. They were individually caged and weighed once a week. The daily dose of amidopyrine was given to the rats with a syringe and a rubber catheter, while the control rats received no drug. Doses which did not produce any other immediate toxic action of the drug were selected for administration, because doses of 25 mgm. and more per kg. weight of the animal were found to reduce their normal temperature. Therefore, smaller doses (not having this effect) of 20 and 15 mgm. per kg. were employed for daily administration. Five rats (Nos. 6 to 10) were given daily doses of 15 mgm. per kg. and the other five (Nos. 11 to 15) were given 20 mgm. per kg. per day. This latter dose corresponds to a dose of 1·4 gm. for an adult human being of 70 kg. weight. The administration was continued, at least, for three months and after three months three rats, one from each group, (control, group on the smaller dose, that on the larger dose) were killed and their bone marrow from the thigh bone was examined. Similarly selected rats were killed at intervals, while the remaining rats (except the controls) continued to receive the drug. Thus the duration of the treatment in the case of surviving animals was about five months.

Blood samples were obtained by clipping the tail with precautions to prevent, as far as possible, infection and undue loss of blood. In fact, we found it necessary to starve the animals from the previous evening to obtain a sufficient flow of blood for our work. Hæmoglobin was determined by Haldane's (Gower's) hæmoglobinometer, the corpuscles were counted in the Buerker type of counting chamber.

Results.—All the animals gained weight during the period of the experiment, including the one (No. 8) that died of pneumonia. It had lost its weight only during the week preceding the death. Reticulocyte counts of all remained practically constant during the whole period. No significant, regular or constant change was observed in the red cell count or in hæmoglobin percentage. Hæmoglobin percentage, more or less, fell in all except three rats (Nos. 13 to 15) which received larger doses. The results of the red-cell counts were very irregular. The white cell counts, however, showed great variations, but these do not appear to be due to the drug, as they were also observed in the controls. In many cases the total white cell counts rose in the average percentage of polymorphs which was about 15% at the outset rose to about 20% at the end of the experimental period, while the average percentage of the lymphocytes which was about 75 to 80 per cent fell to about 70%. Only three rats showed a marked variation. Rat No. 4 (of the controls) showed a temporary rise in the polymorphs (from 15%—20% to about 52%) with a corresponding fall in the lymphocytes (from 70% to 44%) on the 100th day. Rat No. 8 died of pneumonia and before death the polymorphs in its blood increased to 64 %, while the lymphocytes dropped to about 22%. Rat No. 9 also showed an unexplainable polymorpholeucocytosis (49% with 44% lymphocytes) about the 145th day. Bone marrow was not examined at the beginning and the bone marrow examinations were not numerous enough to enable us to draw any conclusions, but they give an impression, if at all, of a slightly increased leucopoiesis, and in some preparations there appeared to be a corresponding diminution of erythropoiesis. But in no case was there any indication of a diminished leucopoiesis.

COMMENTS

In our experiments we did not observe any sign of a depression of the leucocytogenesis and, in this respect, they agree with those of Kracke and of Madison & Squier. The latter workers could produce a drop and antemortem disappearance of granulocytes (after allonal) in only one rabbit but failed to change the blood picture in the other 17 rabbits. Kracke had administered 5 to 10 grains amidopyrine daily by mouth for 45 days and obtained a persistent leucocytosis, while he obtained leucopenia in rabbits after the administration of benzene and certain other drugs. Hoffmann, Butt and Hickey[12] obtained some depression after very large doses (from 0·2 to 0·9 gm. per Kg. weight) of amidopyrine, while our doses corresponded to the medicinal doses of the substance. The results of Holten[10] and his co-workers, published after our experiments were completed, also agree with ours in that no granulopenia was observed by them after administering amidopyrine in doses of 2·5 to 250 mgm. per day to 26 rabbits and 2 guinea-pigs. Thus the attempts to produce granulopenia in animals have, so far, not been very successful and have not supplied any certain evidence of the etiological importance of amidopyrine. But this is not surprising when one considers the enormous amount of amidopyrine consumed and the relatively few individuals afflicted with agranulocytosis, as shown by Dennig's[7] observations already referred to. One is therefore forced to the conclusion that it is the result of a constitutional condition (idiosyncrasy—congenital or acquired) in certain patients rather than of a universal action of the drug. Schittenhelm[14] explains the relative absence of this confliction in Germany by assuming that this idiosyncrasy to amidopyrine which leads to agranulocytosis is very rare in that country.

Amidopyrine is known to be one of the drugs liable to produce idiosyncratic reactions fairly often. The possible question that would arise is whether granulopenia can be recognised as an idiosyncratic symptom, as it is not a hypersusceptibility to the ordinary, for instance analgesic and antipyretic, actions of the drug. The common types of idiosyncrasies mentioned in the books refer to conditions of skin, mucous membranes, circulatory reactions, even retinitis and hepatitis (Sollmann[15]), but according to Schilling[16] blood pictures similar to those in agranulocytosis may be obtained experimentally in anaphylaxis. At present it is not possible to draw a sharp line between the anaphylactic reactions and idiosyncratic reactions, as both have much in common. Holten,[10] in his recent paper, has discussed this question and suggested that agranulocytosis may be a kind of Arthus Phenomenon. He also tried to transfer idiosyncrasy passively but failed.

Although our experiments were undertaken to find out the etiologic importance of amidopyrine in the production of agranulocytosis, a brief reference may be made to the other changes observed in our animals. The changes in the red counts were too irregular to need any comment. The drop in the hæmoglobin percentage was not observed in three of the animals receiving the larger dose. This agrees with the signs of diminished erythropoiesis observed in some bone-marrow preparations. The changes were not marked and since they were not observed in some of the animals receiving the larger dose, the anæmia is probably not of the type observed by Rhodes and Miller in dogs fed on a pellagra producing diet and amidopyrine. The signs of a slight increase of leucopoiesis observed in the marrow preparations agree with the small increase in the percentage of polymorphs seen in the blood of all the animals. It may be a reaction to the injury and some mild infection caused by the clipping of the tail. But this would also [illegible] [illegible] of the leucocytosis observed by Kracke in his experiments. The much greater increase of polymorphs in two rats (Nos. 4 & 9) was probably due to some intercurrent infection, and it was still greater in the one (No. 8) that died of pneumonia. These instances show that the bone marrow of the animals receiving amidopyrine, instead of being depressed, was still capable of reacting by increased leucocytogenesis. Further work is necessary to elucidate the other changes, like anæmia and leucocytosis, observed in the experiments.

SUMMARY

1. Granulocytopenia appears to be the primary cause of agranulocytic angina and other gangrenous lesions.
2. Much available evidence points to intoxication—professional oı medicamentous, to be the cause of the disease, at least, in most of the cases.
3. The evidence incriminating certain drugs as etiological agents is very strong and the use of amidopyrine has produced more cases than any other drug in common use.
4. A therapeutic dose of amidopyrine produces granulocytopenia in patients recovered from agranulocytosis, but the attempts to reproduce the disease experimentally in animals by administering amidopyrine have not been very successful.
5. Our experiments on rats are reported. No granulocytopenia was observed in any of the ten rats given amidopyrine daily for more than three months.
6. There is evidence indicating that granulopenia is not the result of the ordinary toxic action of the drug and that it is an idiosyncratic reaction.
7. It is not yet known whether, besides intoxication, dietetic, hormonic and other etiological factors are associated in the production of granulocytopenia.
8. Further work is necessary to solve these questions and also to elucidate the other blood and bone-marrow changes observed by us.

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STUDIES IN FŒTAL STOMACH AND APPENDIX

(Encl. 4 figures)

By

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During the year 1936-37, I had an opportunity to receive dead fœtuses of varying ages. These I dissected to prepare several specimens for the Embryological Department.

While doing this work, I made certain observations as to the shape of stomach and the position of appendix, and I believe these throw some light on this subject in the adults, and hence this article. Tracings have been taken with the aid of Pantograph from the actual specimens.

STOMACH

Figures I & II are from fœtuses of approximately the same age viz. about 4 months. The stomach of fœtus shown in figure No. I is definitely "J" type. It shows definite formation of the fundus which considerably extends above the level of the incisura cardiaca. Pars Pylorica seems to be separated from the pars cardiaca by definite notch. Pars Pylorica insensibly leads into the duodenum. Comparing the stomach in both cases, the stomach of figure No. II is Disc type, the fundus does not rise much above the incisura cardiaca. The demarcation between the pars cardiaca and the pars pylorica is not apparent on the surface. The muscular coats in the first case were thin, while in the second case were thick. Figures III & IV are from fœtuses of approximately 7 months age. In figure No. III, the stomach is Disc Type, fundus rises only slightly above the incisura cardiaca, there is apparent separation between pars pylorica & pars cardiaca, and there is slight development of pars pylorica. Figure No. IV shows definite fundus formation and greater development in the formation of the body of the stomach, the pylorus is wider compared to figure No. III and can be seen to merge in the duodenum,

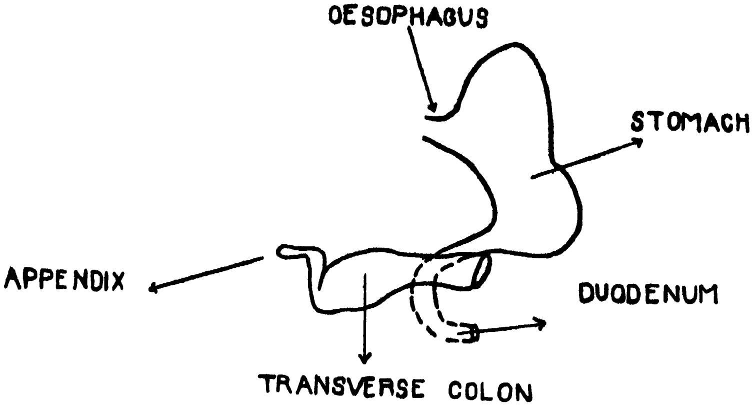

FIG I. from (Foetus 4 months old).

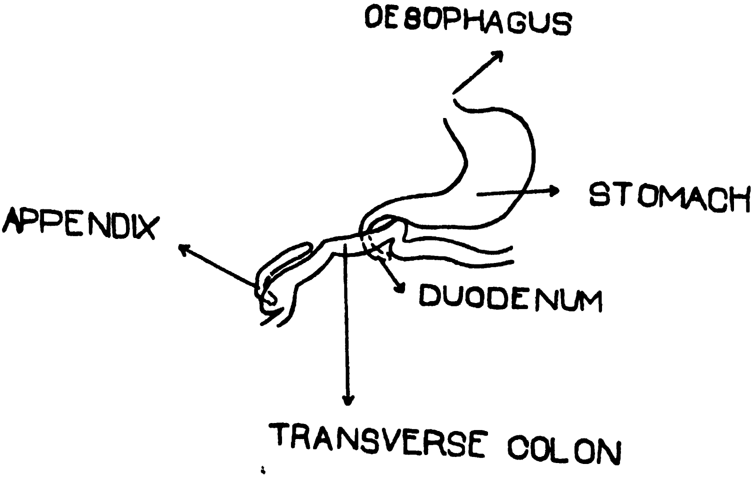

FIG. II. from (Fœtus 4 months old).

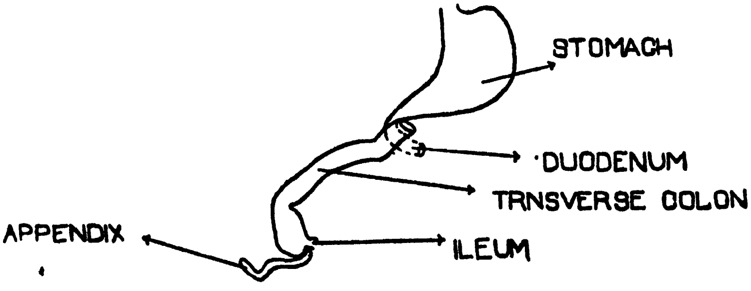

FIG. III. from (Fœtus 7 months old).

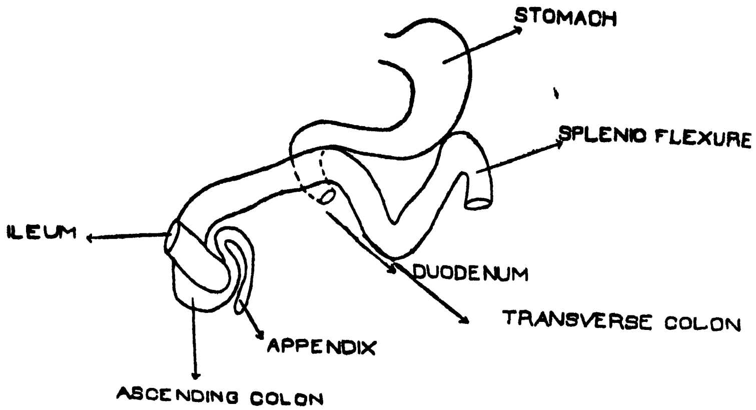

FIG. IV. from (Fœtus 7 months old).

It is usually stated in Text Books of Anatomy that stomach undergoes changes in its shape and size, with the amount of food, change in posture, e.g. erect or reclining, temperament of the individual and pressure of surrounding structures. The facts indicated by the above figures, point out to the possibility of a developmental factor to be also responsible for the variation in shape of the adult stomach.

APPENDIX

In figure No. I, the appendix is bent on the cæcum and is directed to the right, tip lying close to the lateral abdominal wall, the position of the transverse colon and caecum suggests that second rotation has not yet commenced. In figure No. II, the caecum is definitely demarcated from the transverse colon. Joining of Ileum is clearer and appendix is lying parallel and superior to the ascending colon, which is being demarcated from the transverse colon. Second rotation has commenced. In figure No. III, caecum and appendix have descended to the level of the Iliac crest, but appendix is still at right angles to the caecum, though its base is not arising from the apex of the caecum, but from its medial border. In figure IV, the appendix is bent upon itself and recurved, it lies medial and parallel to the ascending colon, its tip nearer to the right testis.

The several positions of appendix suggest that, in addition to a primary rotation around the superior mesenteric artery which brings " U " shaped gut from the umbilical sac back to the abdominal cavity and secondary rotation which results in the formation of ascending colon and descent of the caecum and appendix from the right upper quadrant of the abdominal cavity to the right iliac fossa, certain other movements are also taking place in the Ileo Caecal region to account for the different positions of the appendix in the adult.

These are :—

(*a*) A rotation along the vertical axis of the ascending colon and caecum. This will result in the retro Colic position, as would be the case in the appendix, figured in figure No. II, as also in the appendix figured in figure No. IV, to assume later on mesenteric or splenic or anterior abdominal position of the adult.

(*b*) An anti-clockwise rotation also very likely takes place at the base of the appendix making it assume 11 o'clock, 7 o'clock, 5 o'clock positions in the adults.

The rotations are brought about by the mesenteries fixing the gut to the posterior abdominal wall.

My thanks are due to Dr. P. S. Dastur, for having drawn the above 4 figures from the actual specimens with the aid of the Pantograph.

MEASUREMENT OF INDIAN PELVES

By

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Anybody who has taken measurements of female pelves in Obstetric Wards of Indian hospitals, must have realised that the measurements in Indians differ from the figures given in English Text Books on the subject.

At the suggestion of Professor R. C. Motwani, M. S., I undertook regular and systematic measurements of Indian pelves, both in males and in females. Professor Motwani had also in view the importance of pelvic measurements in Medicolegal cases.

Most of the pelves measurements were taken from fresh Dissection-Room specimens with soft structures in situ. It was not possible to get any appreciable numbers of macerated pelves to draw any definite conclusions. On the other hand the measurements of dissected parts with soft structures in situ gave us the actual diameters of the pelves through which the fœtal head passes during parturition. The total number of pelves measured was 106, out of these 87 were from Dissection-Room specimens with soft structures in situ and 19 were from macerated bodies. Out of 87 from Dissection-Room specimens, 59 were of males and 28 were of females.

The measurements given here are from the Dissection-Room specimens only.

A detailed account of all the measurements of each individual pelvis will be too lengthy a procedure here. I intend to give such a detailed account in some of the journals of Anatomy at a later date. Here I only give averages of some of the measurements, which are likely to be of clinical or medicolegal interest. I am also giving maximum and minimum variations that I have come across.

All of the pelves measured were of Hindus, except 3 in males and 1 in females which belonged to Christians. No deformed pelvis is included in this series.

All the measurements are given in millimetres.

Measurements.	Females.			Males.		
	Average.	Maximum.	Minimum.	Average.	Maximum.	Minimum.
1. Maximum pelvic height.	185	201	170	199	225	177
2. Maximum pelvic breadth.	244	267	228	250	292	213
3. Spinal breadth (between anterior superior iliac spines).	227	249	205	231	257	208
4. Height of Ilium.	122	140	115	131	154	123
5. Breadth of Ilium.	141	153	130	146	163	132
6. Maximum pelvic depth.	150	165	124	144	156	130
7. External conjugate.	176	194	160	176	195	160
8. Upper sagittal diameter.	102	121	80	97	108	82
9. Upper transverse diameter.	109	129	92	108	124	89
10. Lower transverse diameter (Between tips of ischial spines).	93	110	75	81	96	65
11. Right oblique diameter.	111	125	93	105	115	94
12. Depth of pelvic basin.	87	96	60	97	105	85
13. Length of pubis.	79	90	71	78	85	66
14. Length of ischium.	66	75	57	73	82	62
15. Transverse diameter of acetabulum	44	48	40	49	58	41
16. Inner inter tubercular breadth (between the inner aspect of ischial tuberosities)	84	110	69	66	86	52
17. Subpubic angle.	78°	104°	67°	60°	77°	41°

While comparing the different measurements in females and males the following facts emerge :—

The averages of maximum pelvic breadth, spinal breadth (distance between 2 anterior superior iliac spines), depth of pelvic basin and the transverse diameter of acetabulum are greater in males than in females.

The averages of maximum pelvic depth, inter tubercular breadth (between ischial tuberosities), upper sagittal diameter, lower transverse diameter, oblique diameter, and the subpubic angle are greater in females than in males. The external conjugate is same in both. The average of upper transverse diameter and length of pubic is only one millimetre larger in females than in males.

It is clear that on the whole the measurements the false pelves is greater in males. Most of the measurements of the true pelves are absolutely greater in females. Though the difference may not be much but in view of the fact that as a rule, the males have more massive built than females, the relative increase in diameter in females will be greater than the absolute measurements show.

As far as the difference between male and female pelves among Indians, following facts emerge :—

Maximum subpubic angle is 77° in males

Minimum subpubic angle is 67° in females.

Maximum transverse diameter of acetabulum is 48 in females.

Minimum transverse diameter of acetabulum is 41 in males.

Therefore a pelvis showing subpubic angle above 77° *cannot but* be female, while a pelvis showing subpubic angle under 67° must be of a male. Similarly transverse diameter of acetabulum below 41 must be of female while above 48 must be of a male.

Comparison of the measurements of female pelves in this series with those given in Midwifery by Jellet and Mandill.

	English figures	average of present series.
Upper sagittal diameter	110 mms.	102 mms.
Upper transverse diameter	130 „	109 „
Upper oblique diameter	125 „	111 „
Lower transverse diameter	98 „	93 „
(Between spines of ischium inter-spinous)	265 „	227 „
Maximum pelvic breadth	280 „	244 „
Subpubic angle	Rt. Angle	below rt. angle

It shows that all the measurements are smaller than English figures. In upper sagittal diameter there is a difference of 8 mms. while in transverse diameter there is a difference of 21 mms. showing that the female pelvis in Indians is not only absolutely but also relatively narrower than in English females.

The pelvic brim index makes this point clear. Pelvic brim index is $\frac{\text{upper sagittal D} \times 100}{\text{upper transverse diameter}}$. In this series the average as worked out from individual pelvis is 90, while according to figures given above in English females, it is 84.

The greater difference between the inter spinous and maximum pelvic breadth indicates that in Indian females false pelvis is narrower as compared to true pelvis than in English figures.

The lower transverse diameter (between tips of ischial spines) is only 5 mm. smaller than in English figures. This shows that lower part of true pelvis in Indian females is relatively broader (as compared to the upper part) than in English females.

The lower transverse diameter as given in English text books of Midwifery is between the most distant points of the opposite ischial tuberosity. In this series lower transverse diameter is between the two ischial spines, while the distance between the two ischial tuberosities is given as inter-tubercular breadth.

The inter-tubercular breadth in this series is far less than given in English books. This is mostly due to the fact that while in English books the diameter is between the most distant points of the two tuberosities, in this series this measurement is taken between the lowest points of the opposite ischial tuberosities.

In this work I have taken the Laboratory Manual of Anthropometry by H. H. Wilder as my guide.

THE VIABILITY OF CERTAIN PATHOGENIC MICRO-ORGANISMS IN VARIOUS FRESH FRUITS OF INDIA

* *A Preliminary Note*

on

I. *The Viability of V. cholerae in Water-melon.* (*Citrullus vulgaris, Schrad., Tarbuz*).

By

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INTRODUCTION.

It is a matter of common belief that the outbreaks of certain epidemics like cholera usually coincide with certain fruit seasons e.g. the cholera epidemic is associated in certain parts of India with the water-melon season which occurs in the months of March and April ; the dysentery epidemic with papaya fruits. A similar coincidence between the mango season and a dysentery epidemic is reported from Trinidad (Mason : private comm.). At such times the Public Health Officer is asked to trace the source of the epidemic and to take preventive measures for the same. On these occasions the officer depends for some of his preventive measures on the vague and general beliefs of the common people. In the absence of precise data as to the possibility of certain pathogenic organisms thriving on various food-stuffs commonly sold in Indian markets exposed to all possible contamination, this is the only method left to him. Consequently the general measure he adopts is the prohibition of sale of suspected food-stuffs during the epidemic e.g. recently the

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Director of Public Health with the Government of Bombay had prohibited the sale of water-melon during a certain festival.

This lack of precise scientific data on such a vital subject led Lal and Jacob[4] to experimentally find out the values of certain food-stuffs as culture media for V. cholerae and classify them accordingly. Such scientific data so far collected have dealt with *cooked* food-stuffs only and it was thought advisable that similar experiments should now be conducted with *fresh* fruits under conditions as nearly comparable as possible to those prevalent in the market.

In the choice of material for experiments attention had to be paid to the following considerations :

(a) Easy access and cheapness of certain fruits which are readily and in large proportions consumed by the poor class of people.

(b) Whether certain kinds of fruits form good experimental material or not, for there are fruits which are easily attacked by micro-organisms e.g. papaya ; some show an excessive variability of types viz. the mango ; and again there are others which are so markedly acidic as to be totally unsuitable for the growth of bacteria viz. lemons and oranges whose pH are 2·4 and 4·4 respectively.[6]

Water-melon was the first fruit to be selected as an experimental material as a case was reported of the only member of a picnic party who had eaten a water-melon, having succumbed to cholera the next day. Besides, this fruit is very common and cheap during the season and is generally sold in slices by the road-side exposed to aerial contamination.

pH OF THE MELON JUICE

It has been stated by Buchanan and Fulmer[1] that V. cholerae can live only within a certain range of pH as stated below :—

TABLE I.

pH-range of V. cholerae.

Author.	Min.	Max.	Opt.	Range.
Denby (1921)	6·4	7·9	7·7–7·4	1·5
Fennel and Fisher (1919)	5·6	9·6	6·2–8·0	4·0

To verify the above data cholera bacteria were cultivated in a graded series of nutrient broths of different pH-values ranging from 4·2 to 7·1. These experiments confirmed the lower limit of the growth of V. cholerae at pH=5·6 as can be seen from the following table :—

TABLE II.

pH*.	Growth = +
7·0	+
6·8	+
6·3	+
5·6	+
5·2	–
4·4	–
4·2	–

It became also necessary to find out at the outset the pH-range of water-melon juice at different stages of ripeness. For this ten slices of water-melons of varying ripeness were purchased from different shops in the market, ranging from very unripe to over-ripe. pH determinations made of the juice of each slice separately are given below :—

TABLE III.

Slice No.	pH.
1.	4·9
2.	4·9
3.	5·2
4.	5·3
5.	5·3
6.	5·5
7.	5·7
8.	5·9
9.	6·0
10.	6·2

CHOLERA STRAIN

A recently isolated strain was used for the experiments. Its purity was confirmed by the usual carbohydrate and protein reactions as well as serologically i.e. the strain agglutinated to full titre with a mixed Ogawa-Inaba serum.

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* All determinations were carried out electrometrically.

METHODS

The idea underlying all the methods tried was to inoculate the melon, either whole or in slices, with a twenty-four hour peptone-water culture of V. cholerae, incubating at room temperature and obtaining sub-cultures from the inoculated material at intervals of twenty-four hours. The slice method was abandoned after one or two attempts as it was found difficult to prevent contaminants especially fungi. The next method tried was to inject the culture into the whole fruit by means of a hypodermic syringe. This method was satisfactory in so far as pure cultures of V. cholerae could be obtained up to 48 hours but had to be abandoned as sufficient juice could not be withdrawn for pH determinations. To overcome this difficulty, a canula was tried instead of a hypodermic needle. The fruit was supported on a beaker with the inserted canula pointing downwards in the hope that some juice would trickle down. But this failed.

The method finally adopted was as follows. An area was marked off on the fruit, painted with liquid carbolic acid, washed with alcohol and then with saline. A hole was bored on this area with a sterile cork-borer of convenient diameter and plugged with cotton-wool. A later modification was to utilize a sterilized wide glass tube plugged with cotton-wool at one end, the other end being immersed in boiling paraffin and then fixed into the fruit. Thus the fruit could be used like an ordinary culture flask i.e. the inoculum introduced and juice removed by means of a pipette.

The procedure of the actual experiment was as follows. The fruit being prepared as described above, about 3 cc. of the juice was removed and the inoculum introduced. The sterility of the juice was tested according to the method given in the British Pharmacopeia (1932). The pH of the juice was also determined. On the second and subsequent days a few drops of the juice were introduced into peptone-water and the latter incubated at 37°C. for 24 hours after which, a suitable dilution was plated on agar slants for discrete colonies. One of these colonies was confirmed by the usual carbohydrate and protein reactions as well as serologically. The pH of the juice was also determined from day to day. With every experiment a control melon was similarly prepared and the sterility and pH of the juice determined from day to day.

The results obtained by the above technique are as follows :—

TABLE IV.

Expt. No.	Water Melon.	pH.					Cultural Results.				
		at 0 hours.	at 24 hours.	at 48 hours.	at 72 hours.	at 96 hours.	at 0 hours.	at 24 hours.	at 48 hours.	at 72 hours.	at 96 hours.
1	Inoculated	5·0	5·2	6·4			St.	+	Cont.		
	Control.	4·9	5·0	4·9			St.	St.	St.		
2	Inoculated	5·1	5·2	5·2	5·0		St.	+	+	+	Cont.
	Control.	5·2	5·1	5·0	5·2		St.	St.	St.	St.	
3	Inoculated	5·7	5·6	5·8	5·8	5·8	St.	+	+	St.	St.
	Control.	5·3	5·4	5·1			St.	St.	St.	St.	
4	Inoculated	4·8	5·9	6·2			St.	+	Cont.		
	Control.	4·9	6·2	6·2			St.	Cont.	Cont.		
5	Inoculated	5·7	5·5	5·2	5·0	5·3	St.	+	+	+	+
	Control.	5·4	5·3	5·3	5·2	5·5	St.	St.	St.	St.	St.
6	Inoculated	5·5	5·3	5·2	5·4	5·5	St.	+	+	St.	St.
	Control.	5·1	5·0	5·0	5·1	5·3	St.	St.	St.	St.	St.
7	Inoculated	5·3	5·5	6·1			St.	+	Cont.		
	Control.	5·0	4·9	4·9			St.	St.	St.		
8	Inoculated	5·9	6·2	7·6			St.	+	Cont.		
	Control.	5·4	6·4	6·9			St.	Cont.			
9	Inoculated	5·4	5·2	5·0	4·9	5·2	St.	+	+	+	+
	Control.	5·0	4·9	4·9	5·0	5·2	St.	St.	St.	St.	St.
10	Inoculated	4·7	4·7	4·6	4·8	5·0	St.	+	+	+	+
	Control.	4·9	4·7	4·7	4·9	4·9	St.	St.	St.	St.	St.

St = Sterile ; + = V. cholera recovered from culture.
Cont. = Culture overgrown by some other organism or organisms

SUMMARY

Though the experiments are too few in number to draw any general conclusions, certain points of interest are summarised below :—

1. The fruit when bought whole (uncut) proved to be sterile when examined by routine bacteriological methods ; but cultures made from cut slices brought from the market for pH determinations, showed that the slices were contaminated by common dust microorganisms.

2. The maximum period of survival of V. cholerae, when experimentally inoculated into a melon, seems to be four days as far as these experiments go.

3. It has been stated elsewhere that V. cholerae could not grow in nutrient broth at a pH lower than 5·6. This does not seem to hold good for the water-melon juice as we have seen the growth appearing at a pH as acid as 4·7. This seems to show that there is something in the melon which permits the growth of V. cholerae even at pH as low as 4·7, at which it usually dies in an ordinary medium.

4. The pH of the juice of melons both inoculated with V. cholerae as well as those of the controls, remains unchanged for 2 or 3 days—if at all, it falls slightly after the first 24 hours. This state of affairs holds good if the melons are not contaminated by extraneous organisms. In the latter case the pH rises appreciably and abruptly.

In conclusion we wish to thank Lt.-Col. S. S. Sokhey, I.M.S., Director of the Haffkine Institute for the full facilities he has so kindly given to us for our work. To Major R. C. Watts, I.M.S. Assistant Director, Haffkine Institute, our thanks are due not only for suggesting the problem but also for his constant and keen interest in our work ; and finally, Rev. Fr. J. F. Caius, Professor of Chemistry St. Xavier's College, for his critical remarks and suggestions.

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A NOTE ON SOME ABNORMALITIES IN PLANTS COLLECTED IN BOMBAY. II.

(*With 1 Text and 3 Plate figures*).

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In a previous issue[1] of this journal, we had reported on some abnormalities observed in plants collected in Bombay area. Here we describe some further instances of abnormal development, one of which was collected at Castle Rock, during a botanical tour to that place.

Double achene of Anacardium Occidentale, Linn.
N. O. Anacardiaceae.

The specimen described in this paper was found on a botanical tour to Vikhroli, a suburb of Bombay in the Salsette island. As a rule in the Anacardiaceae, the calyx is variously divided, the petals are 3-7 or absent; the stamens are double the number of the petals, rarely equal or numcrous; ovary superior one celled, rarely 2-5 celled, or very rarely the carpels are free; styles 1-3 often widely separated; the fruit is a reniform nut seated on a large fusiform body formed of the enlarged disc and the top of the peduncle.[2] In the present case a double achene was found developed on a fleshy normal peduncle. Similar instances of double fruits have been recorded by various authors[6] from time to time. The achenes were connected with each other on the concave side as seen in Plate I, fig. 1, half way from the base. This condition might have arisen from either[2] two fasciated flowers, or[4] from a single flower having a bicarpellary apocarpous pistil. The latter is most probably the cause of the abnormality and not the former, because, if it were due to fasciation of two flowers, then in that case the peduncle would have some external sign, such as a groove along the long axis or the axis would be flattened as is often found in fasciated branches. The absence of the above mentioned features clearly suggests that it is developed from a single flower.

The Anacardiaceae is classified according to the nature of the ovary, which may be, (*a*) one celled or if two celled, with one cell early suppressed, or (*b*) the ovary may be four or five celled.[3] The genus Anacardium falls in the former group and since we have eliminated the possibility of the double achene being due to the fasciation of two flowers, we come to the conclusion that it must be developed either from a flower having a two celled ovary where both the cells remain fertile, one of the cells not being suppressed as in the normal flowers, or it may have arisen from a flower with a bicarpellary apocarpous pistil both carpels being slightly fused in the development of the fruit.

Triple drupe of Mangifera indica, L.
N. O. Anacardiaceae.

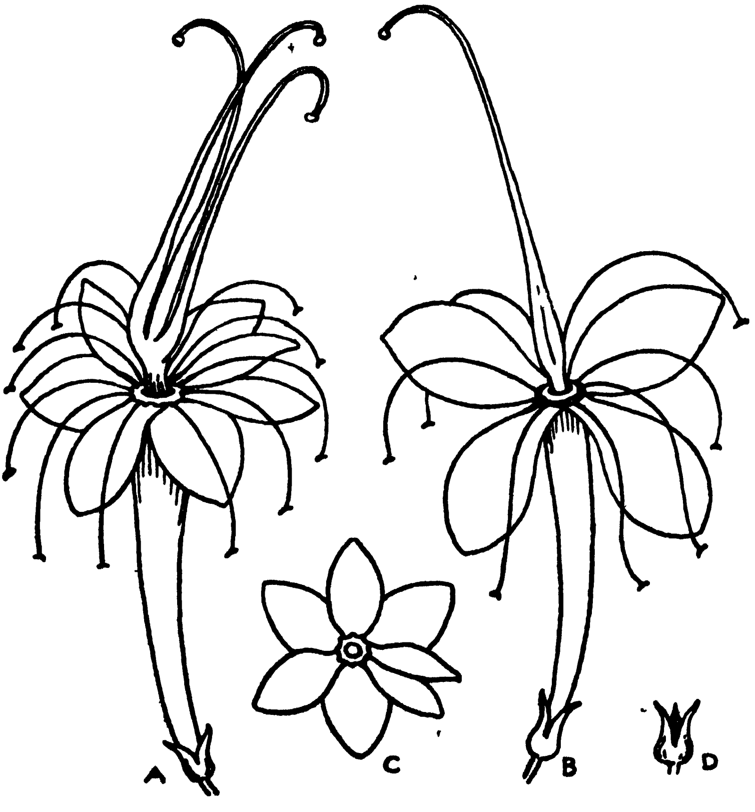
A double drupe of Mangifera indica, L. has been already described by Sinha[7] and Masters[5] and a triple drupe has also been recorded by the former author. The authors over here wish to explain the structure of this triple drupe of mango, which was collected during a botanical trip to Vihar lake in the Salsette island, north of Bombay. The specimen Plate I, Fig. 2. measured 3″ in breadth and 2″ in length. All the three drupes differed in size, one of them the largest, was $1\frac{3}{4}''$ by 2″, the second was $1\frac{1}{2}''$ by $1\frac{2}{5}''$ and the third the smallest was $1\frac{1}{2}''$ by $1\frac{3}{8}''$. The two bigger ones were lying in one plane, while the third smallest was at right angles to the other two. Thus the three drupes were united with each other edge-wise with respect to their long axis. A transverse section of the specimen (Plate I, fig. 3) showed that the two larger ones had developed separate stones, one in each, while the third smallest had developed no stone in it, but there was a distinct loculus, measuring about $\frac{1}{2}''$ in length and $\frac{1}{10}''$ in breadth. According to Sinha[7] the double fruit of Mangifera indica, L. is the result of fasciation of two flowers, but in this case we are of opinion that the double and triple fruits of mango may not be due to fasciation of two or three flowers as the case may be, but may be due to the fact that all the three carpels of a single flower may remain perfect and be fertile instead of one carpel remaining fertile as in the normal flowers. The reason for this conclusion is that both externally and internally there was no indication of fasciation on the peduncle. A transverse section of the peduncle of the fruit showed the normal type of arrangement of the bundles. Similarly there was no trace of a groove on the outside.

Tricarpellary pistil in the flower of Saraca indica. L.
N. O. Leguminosae.

During the month of November 1937, it was found that in one of the corymbs of an Ashoka tree (Saraca indica, L.) in the Victoria

Gardens, Bombay, there were two or three tricarpellary flowers. Though a number of corymbs from the same tree were subsequently examined, no such abnormal flowers were observed. This shows that the abnormality in this plant is of rare occurrence.

The plant in question had produced two flowers of exceptional size and interest (Plate II, fig. 1.) Each of these two were the result of fusion of probably three normal flowers. The abnormal flowers had three bracteoles instead of the normal two (Text fig. 1, d). The calyx tube was flattened and expanded laterally and was more or less solid in nature throughout its whole length and not only at the base as in the normal one. It was crowned by an oblong orange coloured disc instead of a round normal one. The calyx consisted of



TEXT FIG. I.—Flowers of Saraca indica, L.
(*a*) Abnormal flower of Saraca indica, L.
(*b*) Normal flower of Saraca indica, L.
(*c*) Calyx lobes of the abnormal flower.
1. One of the inner segments split into two.
(*d*) Bracteoles of the abnormal flower.

two whorls each possessing three segments, the segments of the inner whorl alternating with those of the outer. One of the segments in the inner whorl seemed to have split into two, so that it really consisted of four segments. Thus the total number of the calyx lobes was seven (Text fig. 1, C). The stamens were eleven in number (Text fig. 1, A) instead of the normal seven to eight (Text fig. 1, B). Instead of a stalked monocarpellary ovary, (Text fig. 1, B) there arose from the disc a stalk bearing three distinct carpels, each consisting of a flattened ovary with styles and stigma. (Text fig. 1, A).

Krishnamurti[4] has cited an instance of Saraca indica, L, bearing flowers with bicarpellary pistils. However these abnormal bicarpellary flowers were like the normal ones in so far as the other organs of the flowers were concerned. The flowers observed here not only differ in having a tricarpellary pistil, but also in the number of the calyx lobes and stamens. All such cases, as these, represent a kind of fasciation. As a result of the study of such striking phenomena exhibited by the fusion of two or three or more flowers, or by the allied cases presented by many peloric flowers, the following suggestions may be put forward.

This precocious development of two or more uppermost lateral flowers may be the outcome of suppression of growth and development of the vegetative apex of the axis (rachis). These flowers not only use up the apical region of the axis wholly but owing to their close proximity, become congenitally united to form a single "apparently perfect" flower, differing from the normal flowers in its much larger size and structure.

Abnormality in the flower of Erythrina indica. Lamk.
N. O. Leguminosae.

Erythrina indica, Lamk. (Coral tree) is very well known for its mode of pollination by humming birds and for its wood used for sword sheaths. The floral formula for the normal flower is K (5), C 5, A (9) + 1, G 1. In the specimen (Plate II, fig. 5) collected in January 1937, from the Victoria Gardens, Bombay, the androecium although monadelphous, is formed of only nine perfect stamens —a departure from the normal fertile ten—the tenth one in this case was a staminode (Plate II, fig. 5, a) having developed a winged expansion. This petaloid staminode had rudiments of anther-lobes which were without any pollen grains. All the other parts of the flower were quite normal both in size and form. A similar abnormal flower has been recorded by Singh[6] where the flower had not only a staminode but had developed an extra vexillum beside the normal one and was also abnormal in size.

Knight and Step[3] have recorded a similar case of transformation of the stamens of Wistaria into petals. They regard all such cases as illustrating that homology of structure which seems to exist between the members of every flower.

An abnormal leaf of Erythrina crista-galli, L.
N. O. Leguminosae.

The abnormal leaf (Plate III, fig. 6) was found developed upon a small tree of Erythrina crista-galli, L. cultivated in the Victoria Gardens, Bombay. Normally, the leaves are trifoliate and petiolate, the petiole varying from two to three inches. Here in the collected specimen (1) the leaf is bifoliate and almost sessile, having a bud in its axil.

Double drupe in Terminalia chebula, Retz.
N. O. Combretaceae.

The specimen was obtained from Castle Rock in December 1936. The normal fruit here is a drupe. In the specimen observed (Plate III, fig. 7) it was found that two fruits had fused together along their edges. On being cut transversely (Plate III, fig. 8) it was found that there were two distinct stones inside a common pericarp. There was a faint line in the middle showing where the fusion took place. It appeared as if the fruit had developed from a double fasciated flower. The base also showed the scars of the fused peduncles with the separate vascular rings entering the fused fruit; Masters[5] and Sinha[7] have described the same type of abnormality in the fruit of Mangifera indica, L.; but the former found two seeds united together in his specimen. The latter, however, has described an abnormal specimen of Mango fruit very similar to what has been observed here in Terminalia chebula.

SUMMARY.

Abnormalities in the following plants were observed :—

1. Double achene of Anacardium occidentale, Linn. N. O. Anacardiaceae.
2. Triple drupe of Mangifera indica, L. N. O. Anacardiaceae.
3. Tricarpellary pistil in the flower of Saraca indica, L. N. O. Leguminosae.
4. Abnormality in the flower of Erythrina indica, Lamk, N. O. Leguminosae.
5. An abnormal leaf of Erythrina crista-galli, L. N. O. Leguminosae.

6. Double drupe in Terminalia chebula, Retz. N. O. Combretaceae.

Where possible it has been attempted to elucidate the causes of these abnormalities.

ACKNOWLEDGMENT.

We wish here to express our indebtedness to Mr. H. S. Dalal for his kind help in taking the photographs.

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PLATE I

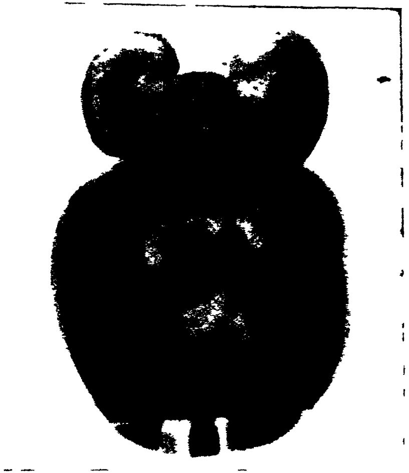

FIG. 1

Double achene of Anacardium occidentale, Linn

FIG. 2

Abnormal fruit of Magnifera indica L

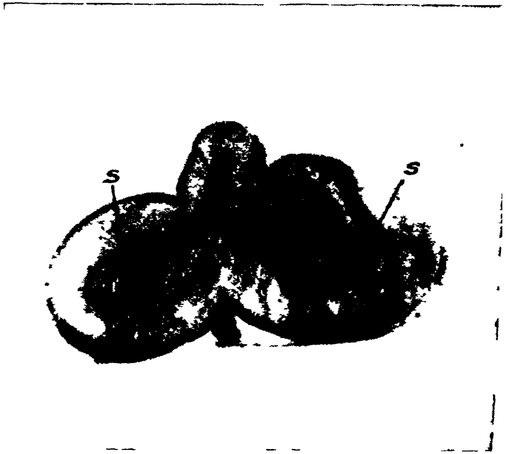

FIG. 3

T. S. of the abnormal fruit showing the three celled structure. Seed (s) develops in the two cells only.

PLATE II

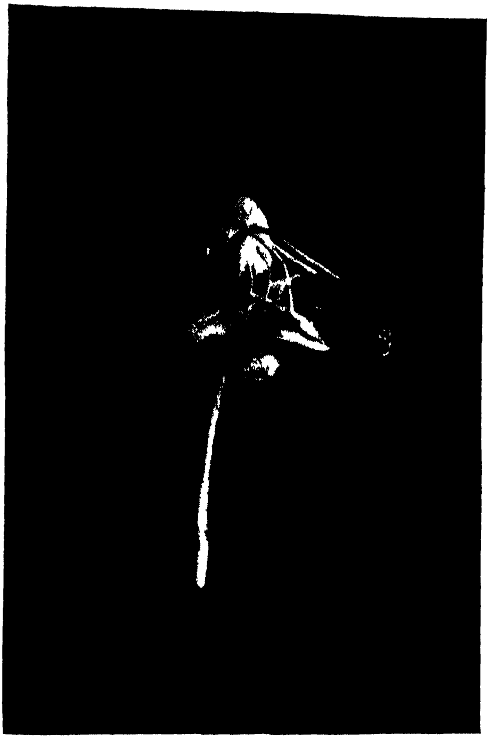

Figure 4. Abnormal flower of Saraca indica, L.

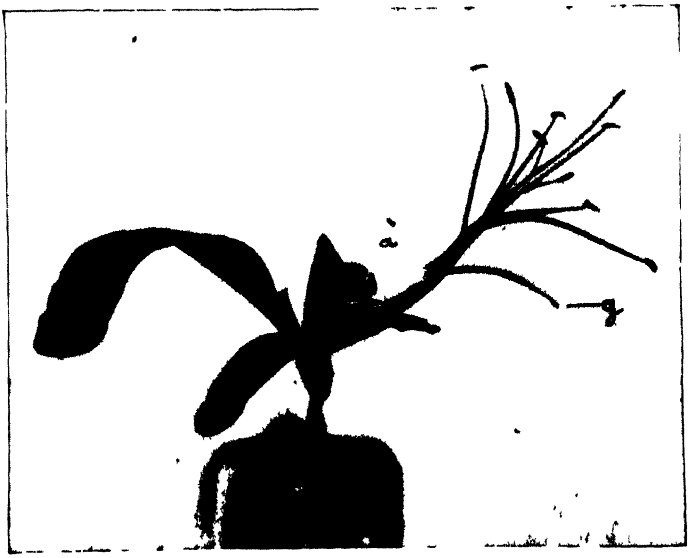

Figure 5. Abnormal flower of Erythrina indica, Lamk., showing petaloid stamen (a), gynaecium (g), and nine fertile stamens.

PLATE III

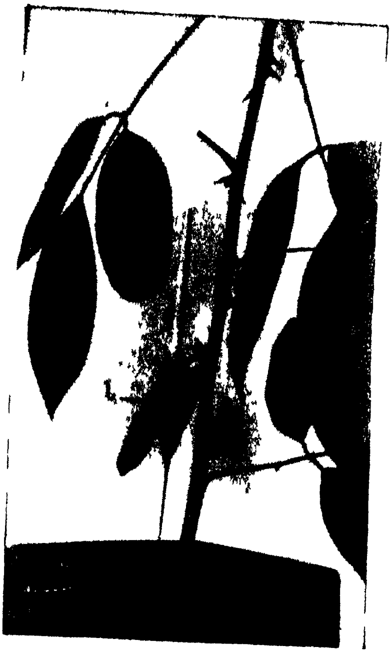

Figure 6 A branch of Erythrina crista-galli, L showing a bifoliate-leaf (1)

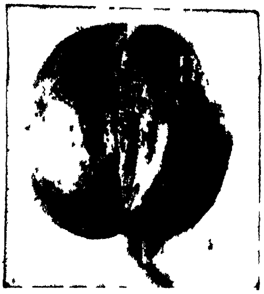

Figure 7. Double drupe of Terminalia chebula, Retz

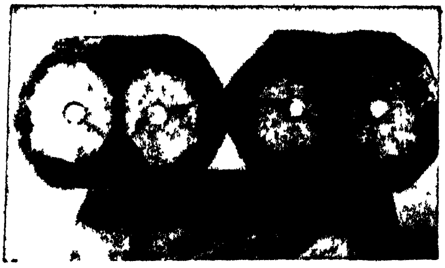

Figure 8. T. S. of the Double drupe of Terminalia chebula, P Ret

BULBILS OF REMUSATIA VIVIPARA Schott.

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and

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(*With 1 plate and 5 text-figures.*)

CONTENTS.

		Page
I.	Introduction	47
II.	Description	47
	A. Adult plant	47
	B. Bulbiferous shoot and the bulbils	49
	C. Germination of the bulbils	52
III.	Theoretical considerations	54
IV.	Summary	55
V.	Literature cited	56

I. INTRODUCTION.

During our short stay at Lonawala in August 1935, the senior author observed some curious shoots on the corm of an aroid, growing on the bark of a mango tree in a deep ravine at Khandala. The shoots were full of small buds recalling to one's mind the appearance of vivipary. On critical examination, however, they turned out to be bulbils only.[1] As this interesting aroid is not of common occurrence, we propose to give here an account of the structure, development and germination of the bulbils found on it.

II. DESCRIPTION.

A. Adult plant.

The plant is an annual, usually an epiphyte growing in the clefts of trees in the Ghat jungles.[2] It appears in the monsoons only. Its stem is a small pink-coloured corm bearing few leaves every season. From the periphery of the corm sprout up three to five phototropic shoots and they bear the bulbils (Plate I, Text-fig. 1). The bulbiferous shoots are hollow and corky. They have only the scaly leaves on them. Bulbils arise in the axils of these scaly leaves and have to pierce their way through them (Plate I. Fig. 1). In October, the shoots dry up and the bulbils either fall in the vicinity of the parent-corm or get dispersed by wind and animal agencies. The number of bulbils produced on a single plant is very large ; for example, on one occasion we collected something like 700 bulbils in the vicinity of a single plant.

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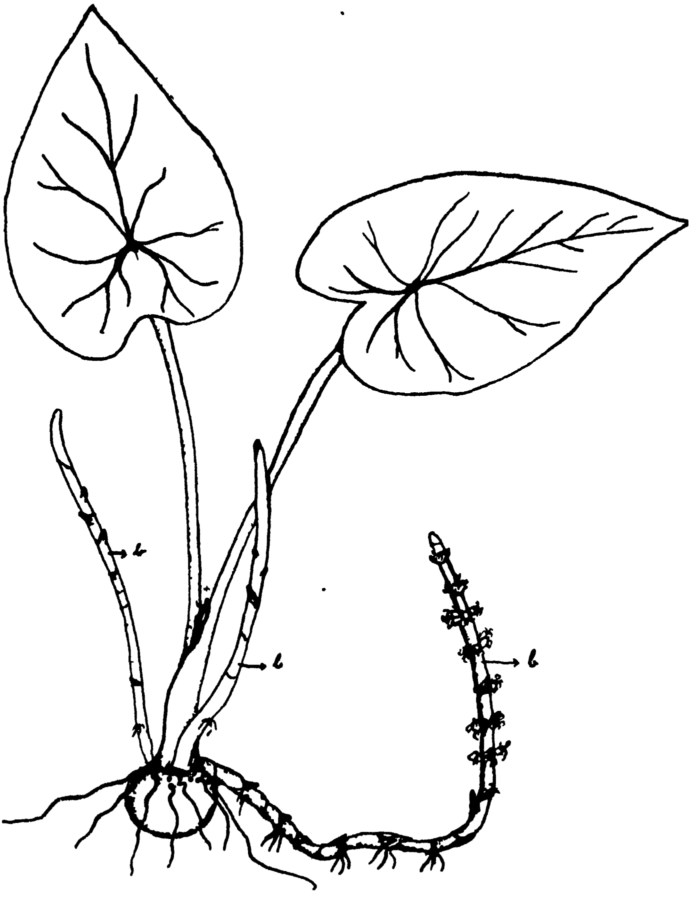
[1] Evidently the plant owes its wrong name to spurious appearance of vivipary presented by the bulbils on shoots.

[2] Cooke (1909), p. 828; Hooker (1894), part VI, p. 521.



TEXT-FIG. 1.—Adult plant of *Remusatia vivipara* Schott. Note the rounded corm with three bulbiferous shoots *b* on it. (¼ Natural size)

The localities where this aroid occurred were visited all the year round to see whether the plant produced any flowers some time during the year but never we found it to do so. This has also been the experience of other workers. Prof. H. G. Champion who had seen the plant in forests at the foot of the Himalayas informs us that he too had never seen any flowers on the plant. At Courtallam in the Madras Presidency the gemma-bearing form is found in plenty but the flower producing form is 'exceedingly rare'.[1] Goebel[2] suggests that the flower-producing form might be found in localities other than those of the gemma-producing form. But to the best of our endeavours, we could not get the flowers on plants growing in quite different conditions and at different places in the Presidency. Thus for example, the plants transferred to Poona, and Ahmednagar (rather a dry, non-hilly place)—continued to produce the bulbils only.

B. Bulbiferous shoot and the bulbils.

Each bulbiferous shoot has 20-30 nodes (Plate I, Fig. 1). The lower six to eight nodes do not bear the bulbils but only the adventitious roots. The upper 15-20 nodes bear bulbils in the axils of the scaly leaves, more or less horizontally (Plate I, Fig. 1). At each node there are about 20-30 bulbils. On an average a single plant of *Remusatia vivipara* is thus capable of giving rise to a varying number of bulbils from 900-1125. This is perhaps the largest number of bulbils recorded from a single plant. All the bulbils do not appear to undergo germination since the plant is not very frequent even in its natural habitats.

Each bulbil is 0·2—0·6 cm long, half as much broad, oblong or squarrose, covered with 10-20 scales (Text-fig. 2). Each scale has a prominent midrib merging into a pointed, hooked apex—the catching organ of the bulbil (Text-fig. 2B). The centre of the bulbil is occupied by an undifferentiated stem full of starch and other reserved food material. From the axils of the lower scales come out the rudiments of roots, and sometimes secondary bulbils also (Text-fig. 2C). The cells in the scales are full of a brown pigment, raphides and storage tracheids in the basal region.

Arrangement of the scales in a bulbil is shown in the Text-fig. 2-1. It will be noticed that it is somewhat similar to the arrangement of leaves in the bulbils of *Lycopodium clavatum* described by Goebel. But it will also be noted that it is not identical with it. The twisting

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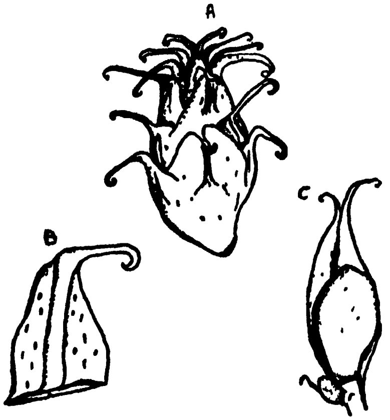
1. Wight, Icones de Plantarum, t. 798.
2. Goebel (1905). part II.

of the inner and the outer leaves, the lower leaves in particular, is quite common in the bulbils of many species of *Lycopodium*, e. g., *L. lucidulum*, *L. nummulariformis* etc. But in the bulbils of *Remusatia vivipara* the inner leaves do not undergo distortion due to their scaly nature. The lower leaves in the bulbils in *Lycopodium* as well as *Remusatia* are developed asymmetrically, and this results in the horizontal lie of the bulbils at maturity.



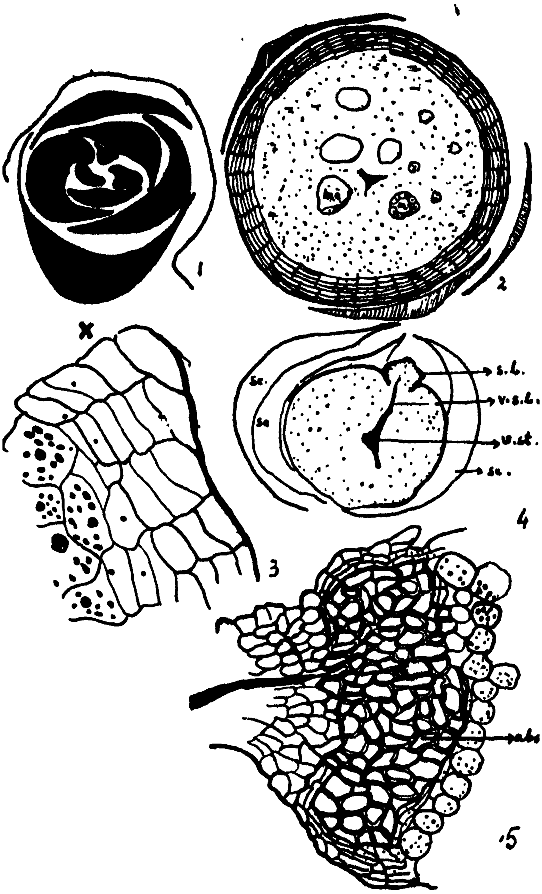
TEXT-FIG. 2.—Bulbil of *Remusatia vivipara* Schott. A-entire bulbil with hooked tips; B-a single scale on the bulbil showing midrib and the hooked apex; C-a bulbil with another bulbil in the axil of a lower scale. × 26.

The internal structure of the bulbil shows the following peculiarities in a transverse section :—

Below the outer epidermal layer lies a massive cork-cambium similar in appearance, function and position to the corky layer in the bulbiferous shoot which bears it (Text-fig. 3-3). Below that is the cortex full of starch and other substances. A rudimentary vascular strand passes in the centre from the base towards the apex, and loses its identity in that region. The large cavities in the cortex are the mucilage canals.

The Text-fig. 3-4 is a transverse section of the bulbil passing through the lower region. Here it will be noticed that there is another small bulbil in the axil of the lower scale and that the vascular supply to the latter is from the vascular strand of the former. A section passing below this region brings out a loose parenchymatous tissue at the base of the bulbil, structurally and functionally similar to the abscission layer, found at the bases of the leaves of *Juglans.*

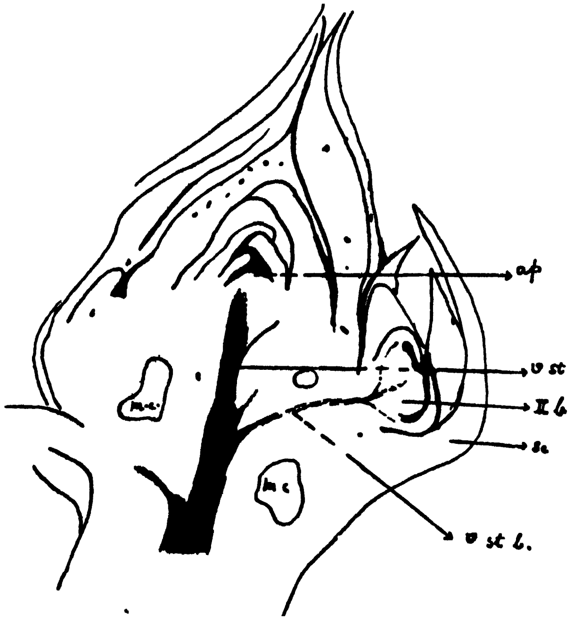
Prunus and *Acer* at the time of leaf-fall. A radial longitudinal section brings out this tissue more clearly (Text-fig. 3-5).



TEXT-FIG. 3.—Internal structure of a bulbil of *Remusatia vivipara* Schott. 1—Arrangement of scales in a bulbil; 2-T. S. of the bulbil showing the outer corky layer and cortex full of reserve food material and mucilage canals-*m.c.*; 3-T. S. of the corky layer (magnified); 4-T. S. of the bulbil in the lower region: note the secondary bulbil-*s.b.* developing in the axil of a scale-*s.c.*, vascular supply to the secondary bulbil-*v.s.b.* from the central vascular strand-*v.st.*; 5-Radial longitudinal section of the bulbil showing 'abscission layer'-*abs.* × 58.

The Text-fig. 4 is a median longitudinal section of a bulbiferous shoot passing through apex. The apex of the shoot (Text-fig. 4, ap) lies below numerous sheaths of scaly leaves. To the right is a bulbil in formation. The vascular strand of the shoot sends off a branch to the bulbil—which is being formed. The origin of the bulbil is clearly axillary. There is nothing in the development of the bulbil at this stage or at any later stage that could suggest the possibility of perianth. Evidently the primordia of the bulbils are not derived from the primordia of the flowers as in the case of *Globba bulbifera* but merely from the shoot-primordia in the axils of the scaly leaves.

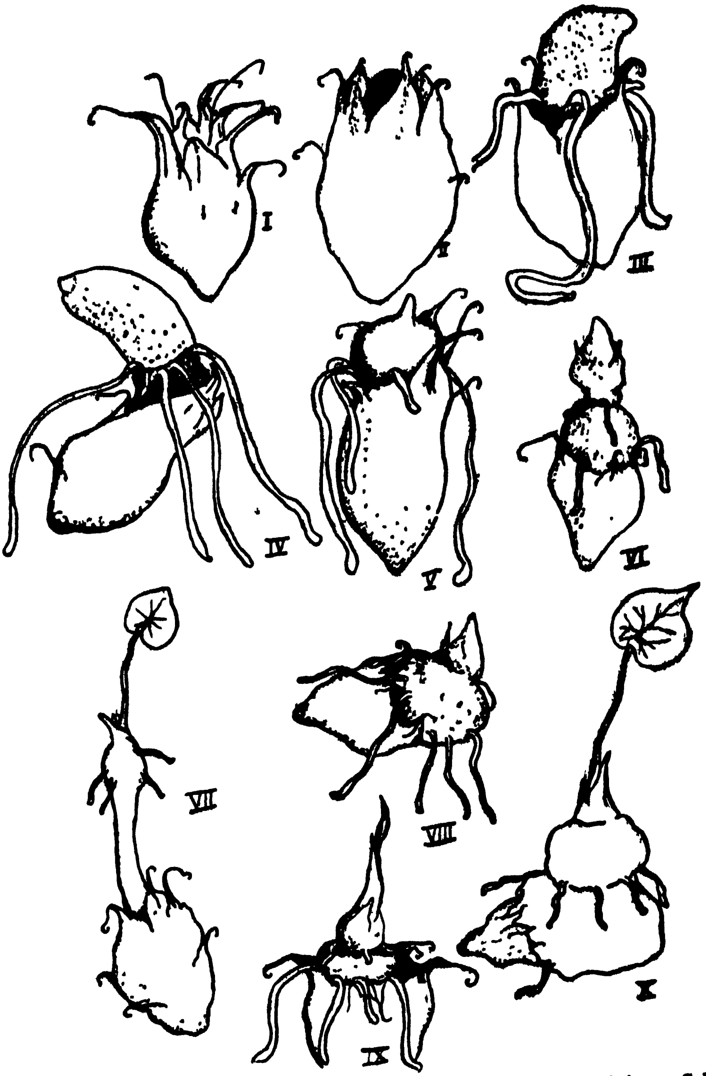
To recapitulate, the main structural features in the bulbils of *Remusatia* are: hooked tips of the covering scales, origin from the axillary shoot-primordia, corky layer at the periphery, abscission layer at the base, and undifferentiated stem in the centre, full of starch reserve.



TEXT-FIG. 4.—Median longitudinal section of the apex of a bulbiferous shoot of *Remusatia vivipara* Schott showing a bulbil developing in the axil of a scale and its relation to the apex of the bulbiferous shoot. *a.p.*, apex of the bulbiferous shoot covered with numerous scales; *s.c.* a scale bearing a bulbil in its axil; II*b*.-a bulbil in formation; *v.st.*—vascular strand of the bulbiferous shoot; *v.st.b.*—vascular supply to the bulbil arising from the vascular supply of the bulbiferous shoot; *m.c.*-mucilage cavities. ×35.

C. Germination of the bulbils.

The bulbil gets easily detached from the parent-shoot even with a gentle pressure, and is carried over to new situations by wind, bird and other animal agencies. It sticks to its new site by means of its hooked tips till the advent of next monsoons and begins to germinate thereafter. Its course is followed through many transitional



TEXT-FIG. 5.—Germination of the bulbils of *Remusatia vivipara* Schott. × 26. For explanation see text.

forms shown in Text-fig. 5. First of all the lower scales on the bulbil decay and the central stem swells (Text-fig. 5 I). The storage tracheids at the base of the scales become turgid and the tips diverge. The apex of the bulbil pushes its way through them and peeps out (Text-fig. 5 II). The apex now being exposed to sunshine turns green. The root-primordia which sometimes develop even before the bulbil is detached from the parent shoot, come out and anchor the bulbil to substratum (Text-fig. 5 III). The major part of the stem is still concealed in the midst of the scales (Text-figs. 5 III, IV). The stem is then gradually drawn out and begins to elongate. It bears a few ephemeral scales only. Very often the growth of the bulbil stops at this very stage for the season and the bulbil aestivates. It is quite likely that it may be dispersed even after this stage of its growth, as the hooks are still in tact in the upper region. The bulbil resumes its growth next year and forms either an elongated portion of the stem as in the Text-fig. 5 VII or a rounded one as in the Text fig. 5 V, VI, VIII, IX. The first vegetative leaf appears and no more metamorphic changes occur henceforth. The two portions of the stem formed in two years gradually get super-imposed and form a characteristic corm—the adult stem of the plant (Text-fig. 5 IX,X). Connection of bulbil after this stage is merely vestigial and is finally cut off.

III. Theoretical considerations.

One of the striking peculiarities in the life-history of *Remusatia vivipara* is the deletion of the flowering stage substituted by the production of a large number of bulbils. This change in the life-cycle of the plant is not due to any interference on part of man but is largely a result of the physical environments of the plant. *Remusatia* has to complete its life-history in rains, so heavy in the Ghats. For days together there is no chance for a beam of sunshine to penetrate through the clouds and accelerate the growth. Water-logging is common—a condition particularly adverse to the young roots. Under these circumstances it is to be doubted whether a seedling of *Remusatia* will survive better than a gemma, which *ab initio* inherits the same qualities as the parent plant and hence better fitted for the conditions in which the plant has to live from year to year. This is perhaps one of the reasons why the plant is so slow and shy to produce the flowers.

We may next enquire what is the morphological nature of the bulbils in question. The bulbils in *Remusatia* arise in the axils of the scaly leaves; they have a corky layer at the periphery; they bear secondary bulbils in their axils; they have meristematic tissue at the apex; they never show anything like perianth at any stage in their formation; all these characters lead us to conclude that the bulbils in *Remusatia* are derived from the primordia of the shoots like *Lycopodium* and not from the primordia of flowers as in the case of *Globba bulbifera, Globba racemosa* or *Agave bulbifera etc.* The bulbils of *Remusatia* although agree in their morphological nature with the bulbils of lycopods, they differ from them in one important particular, viz. the organs used for the storage of food-material. In the bulbils of lycopods the food material is stored in fleshy leaves whereas in the bulbils of *Remusatia vivipara* it is stored in the axis itself.[1] Now a storage stem in which the leaves are thick and fleshy is called a bulb and a storage stem in which the axis becomes fleshy—the leaves being reduced, is called a tuber. It will be seen that the bulbils of *Lycopodium* correspond to the former catagory while the bulbils of *Remusatia* and *Dioscorea* correspond to the latter catagory. It is better, therefore, to call the bulbils of *Remusatia* and *Dioscorea,* the *tuberous* bulbils while those of *Lycopodium,* the *leafy bulbils.*

IV. SUMMARY.

The paper gives an account of the bulbils of an aroid, *Remusatia vivipara* found in the clefts of trees in the Ghat jungles. The aroid is an annual, which thrives in the monsoon only. It does not produce flowers but a large number of bulbils instead. This anomaly in the life-cycle of the plant is very probably the result of the peculiar circumstances under which the plant lives.

The bulbils are borne in clusters, on three to five phototropic shoots springing from the periphery of the corm. Their number is surprisingly large. A single plant of Remusatia may bear as many as 700-1000 bulbils in a season ; probably the largest number recorded from a single plant. They are protected by means of scaly leaves having recurved tips. These are the catching organs of the bulbil and help it in its dispersal. Sometimes secondary bulbils are found in the axils of the lower scales of a bulbil.

Internally the bulbil is characterised by an outer corky layer, apical meristem as in a stem, massive cortex full of starch and other substances, rudimentary vascular strand and an abscission layer at the base. With all these structural peculiarities, the bulbil is highly adapted for the purposes of dispersal by wind and animal agencies.

Developmentally the bulbil is derived from the primordia of the axillary shoots as in many species of *Lycopodium,* and not from the primordia of the flowers as in *Agave bulbifera* or *Globba racemosa.* In the bulbils of lycopods the food is stored in the leaves whereas in the bulbils of *Dioscorea* and *Remusatia* it is stored in the axis. It is, therefore, suggested by the authors that the bulbils

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1. This is also true of the bulbils of *Dioscorea.*

of lycopods should be classed as *leafy bulbils* and those of *Remusatia* and *Dioscorea* as the *tuberous* bulbils.

The course of germination of a bulbil in *Remusatia* is followed through transitional forms, gradually elaborating upon an undifferentiated nepionic stem, leading to its adult stage viz. the corm.

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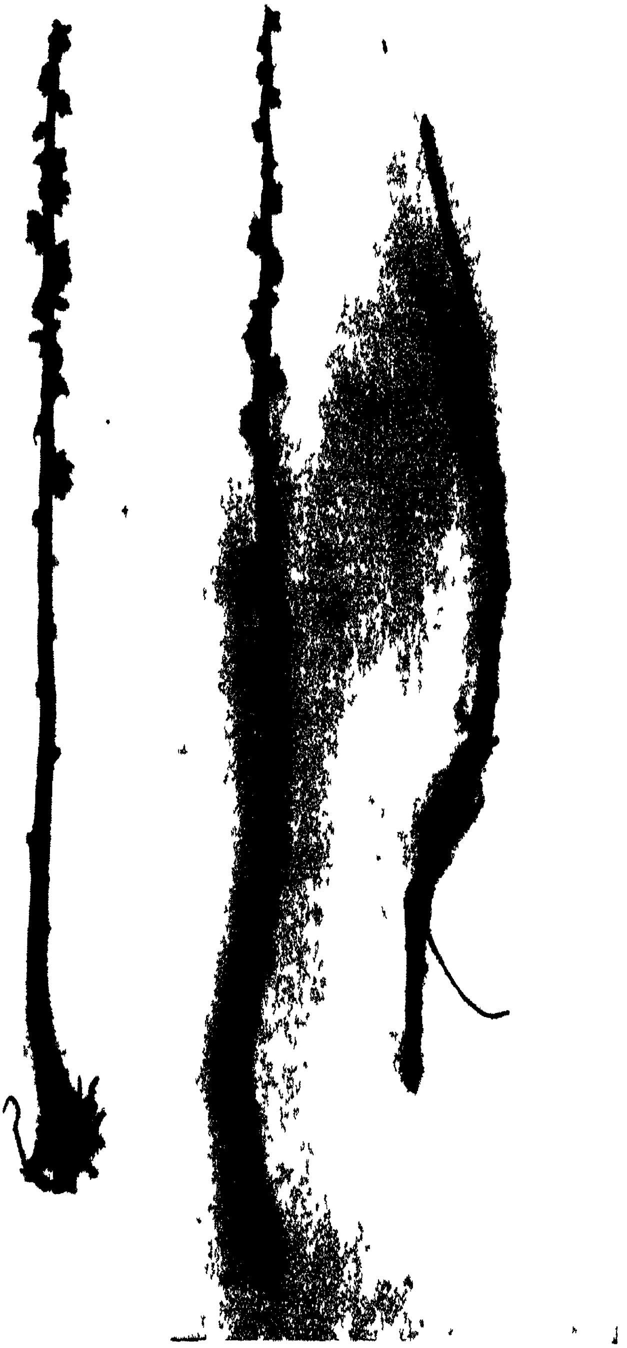

PLATE I, FIG I—Bulbiferous shoots of *Remusatia vivipara Schott* (½ Natural size)

PHYLLODY IN THE FLOWERS OF CROTALARIA STRIATA, DC.
N. O. LEGUMINOSAE.

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In the studies on the abnormalities in plants, it is necessary to compare the abnormal specimens Fig. 1B. with the one of the normal Fig. 1A. order, and hence it will not be out of place to describe the normal plant in question.

Crotalaria striata, DC,[1] is a herb belonging to N. O. Leguminosae, sub-order Papilionaceae. It is about 2-3 feet high; stem stout and more or less striate; the young branches silky. Leaves membranous; petioles $1^1/_8$-3 in. long, stout and slightly pubescent; stipules very minute. Leaflets 2-3 by 1-$1^1/_8$ in. elliptic, obtuse or acute, glabrous above and minutely puberulous and glaucous beneath. Flowers numerous, in erect terminal and lateral racemes, which sometimes reach one foot long; pedicels short; bracts setaceous. Calyx $\frac{1}{4}$ in. long, teeth as long as the tube. Corolla dull yellow, veined with purple, twice as long as the calyx. Pod $1^1/_8$-2 in. long, much deflexed, oblong cylindric glabrous, and shortly stalked. Seeds 20-30 dark brown.

In normal flowers the sepals, petals, stamens, and pistil occupy definite position, but under abnormal conditions, brought about either by the presence of a parasite, virus, insect bites, or some physiological disturbances brought about by various external factors, one type of floral organ may be transformed into another or into ordinary leaves. Stamens may become leafy as in Pennisetum typhoideum[4], petals may turn into sepals, stamens into carpels and carpels may become leaf-like as in some crucifers.[4] To this, the term 'Phyllody' is applied, meaning the change of the floral organs into leaf-like structures.

Transformation of carpels and stamens into leaves is very common in the Leguminosae, as, in Trifolium ripens,[2] Trifolium alexanderinum Linn.[6] In the former specimen, the carpels especially are more or less changed; they are either enlarged and inflated or in the place of each carpel a foliage leaf appears; while in the latter, all parts of the flowers except the sepals get transformed to a varying extent into types of leaves ranging from mono- to tri-foliate. In the specimen of Crotalaria striata, DC. over and above the occurrence of phyllody there was an alternation in symmetry. The plants were distinctly pale in appearance and diminutive in size in contrast to the normal healthy plants, with excessive branching accompanying the dwarfing. Changes in the size and shape of the leaves were also noticeable. They showed curling due to unequal development of larger leaf areas or surfaces; blister like elevations with intervening chlorotic depressions, thus giving the leaf surface rugose wrinkled appearance. The flowers were reduced in size and they showed the following striking changes in corolla, stamens, and carpels. The sepals were five in number, they deviated from the normal ones. Petals were like sepals, green in colour and they varied in number from 3-5 usually the latter. In the latter case there was no differentiation of segments into standard, alae, and keel or carina. All the parts were alike and more or less leafy in nature.

The stamens exhibited a marked deviation from the normal ones in size, number and cohesion, and some of them appeared as diminutive foliage leaves. There were some with both the anther lobes developed externally but without pollen; and there were a few in which a 'four winged' leaf (Text Fig. C.) was developed. This can be well explained as given under :—

According to Goebel[3] a young stamen before its birth is a four angled body and in each of the angles, the primordium of an archesporium is differentiated. The primordium of each angle by cell division and growth ultimately develops into a small leaflet. Such phyllody of stamens is a phenomenon of growth which is altogether abnormal when compared with the usual conditions and which is generally found in vegetative leaves.

Two factors seem to play an important part in bringing about the transformation of the primordia of the stamens into leaf-like structure. First, the stage of development of the primordium is to be considered at the time when the impulse is transmitted and secondly the strength of the impulse, for both these factors go to determine whether the primordium will result into a simple or a four-winged foliage leaf, or petal, or such a leaf with more or less malformed pollen sacs.

TEXT-FIGURE I.

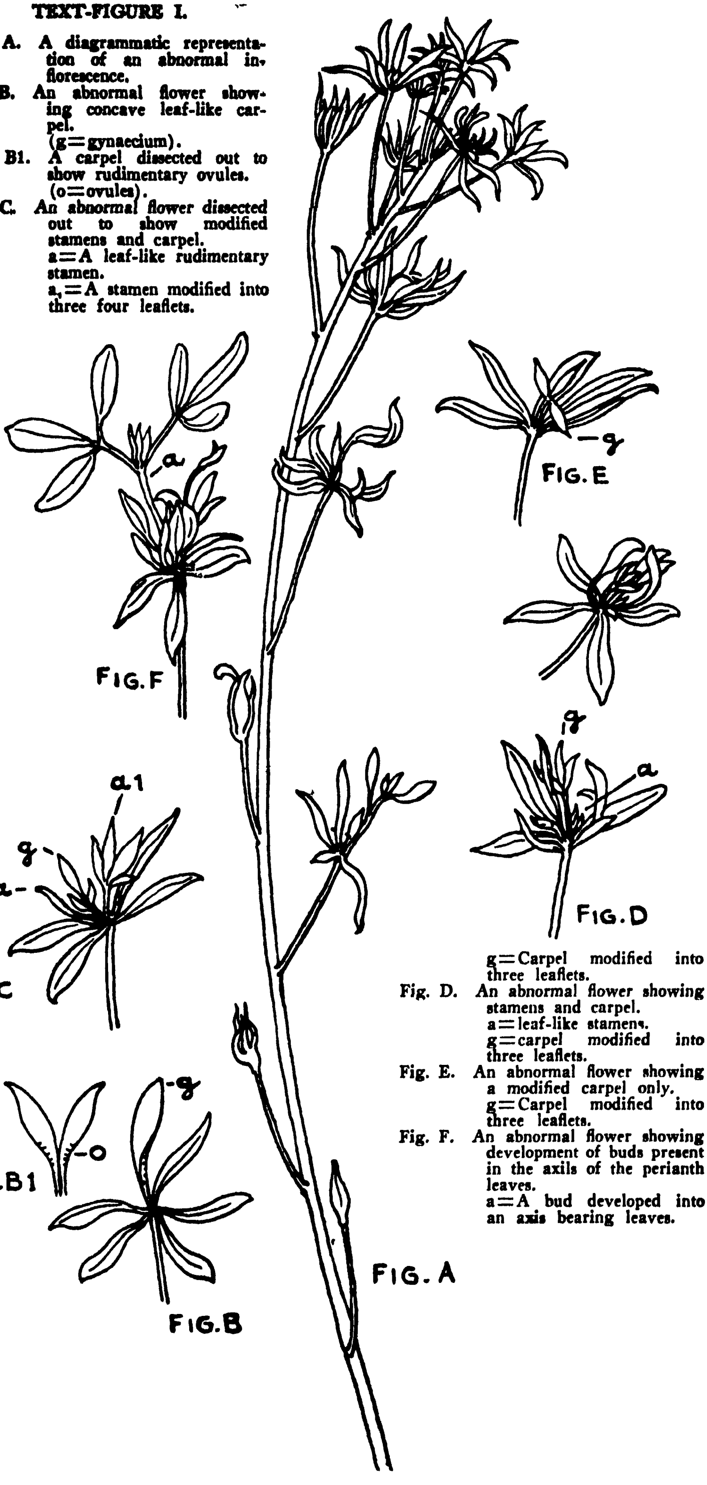

Fig. A. A diagrammatic representation of an abnormal inflorescence.

Fig. B. An abnormal flower showing concave leaf-like carpel.
(g = gynaecium).

Fig. B1. A carpel dissected out to show rudimentary ovules.
(o = ovules).

Fig. C. An abnormal flower dissected out to show modified stamens and carpel.
a = A leaf-like rudimentary stamen.
a_1 = A stamen modified into three four leaflets.
g = Carpel modified into three leaflets.

Fig. D. An abnormal flower showing stamens and carpel.
a = leaf-like stamens.
g = carpel modified into three leaflets.

Fig. E. An abnormal flower showing a modified carpel only.
g = Carpel modified into three leaflets.

Fig. F. An abnormal flower showing development of buds present in the axils of the perianth leaves.
a = A bud developed into an axis bearing leaves.

Another interesting feature noted, is the bud formation in the axils of the perianth leaves and stamens; these buds developed into foliage shoots in three or four cases. (Text Fig. F.)

The carpels of all the flowers, borne on the abnormal inflorescence had become transformed into varying degrees. They showed complete phyllody and the formation of ovules was entirely suppressed. The carpels showed the following variations :—

1. In the most abnormal flowers the carpel was raised on a stalk, which varied in length from $(\frac{1}{8}-\frac{3}{4})$ inch.

2. The carpel in some was a single boat shaped concave leafy structure (Text Fig. B) with or without some little protuberances on the margins (rudimentary ovules).

3. In others it was like a miniature leaf, i.e. it was trifoliate, the middle leaflet a bit bigger in size and boat shaped, the two lateral small and membranous; in some flowers they could be made out by the help of a lens.

The above specimens of phyllody clearly suggest that the stamens carpels are nothing but highly modified forms of foliage leaves, though they often differ from foliage leaves in their external configuration. According to Sachs[5], the difference in the form of the organs of plants are based on their material differences and the changes of organic form are in touch with changes in the process of nutrition. In malformations one organ may appear instead of another as the primordium of one organ may wander into that of another. In flowers, therefore, since the different organs lie so close to one another, very slight disturbances can easily cause such interchanges of organ forming material. The latter may be the whole mass of material forming the organ like the differences in the carbon-nitrogen ratio or small quantities of chemical substances which may act as ferments on the plastic substances which flow into the growing points and these react for the formation of particular organs.

SUMMARY.

The phyllody of the flowers of Crotalaria striata, DC. is described. It is suggested that petals, stamens, and carpels are highly evolved types of leaves, though they often differ from foliage leaves in their configuration. These variations are clearly due to interaction of unknown factors, bad nutrition, or parasitisms etc. Thus

PLATE 1

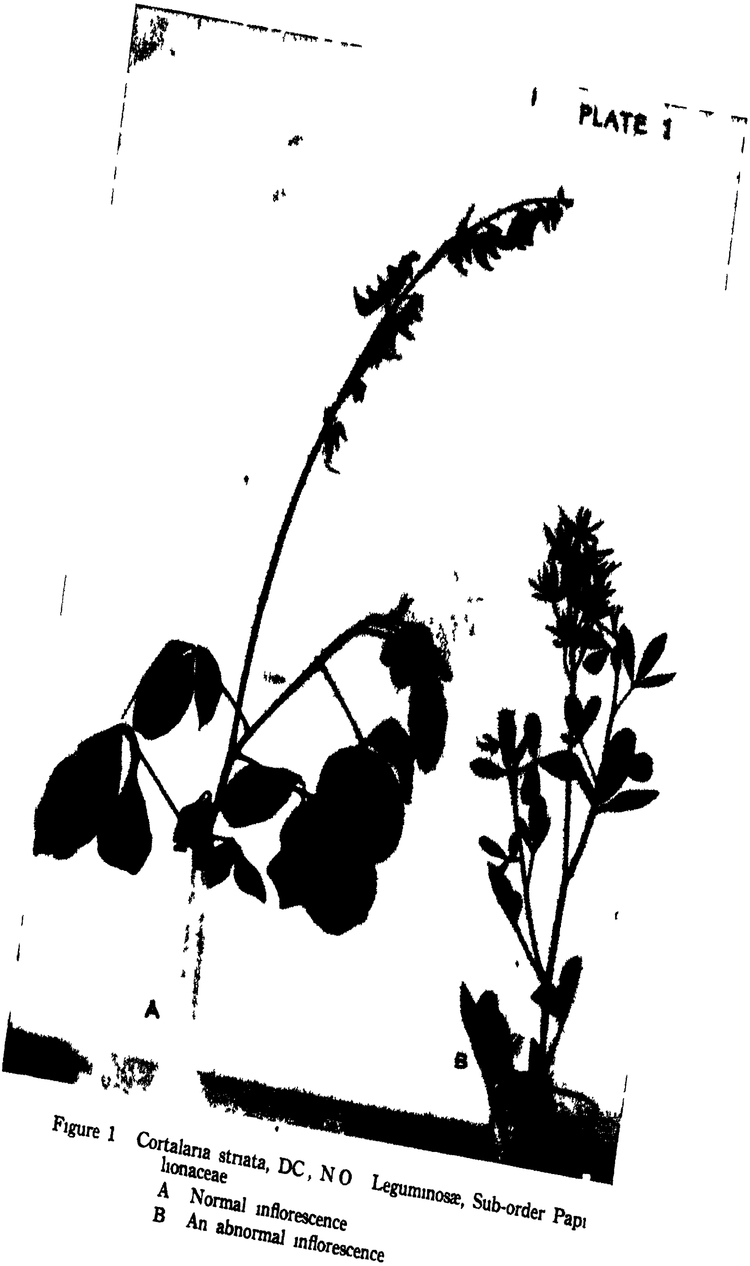

Figure 1 Cortalaria striata, DC, N O Leguminosæ, Sub-order Papilionaceae
A Normal inflorescence
B An abnormal inflorescence

the phyllody of flowers in general is a symptom of disease, it is misbirth, the exact cause of which is not known in many instances.

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STUDIES ON THE VASCULAR CRYPTOGAMS OF THE BOMBAY PRESIDENCY.

PART I.—DISTRIBUTION OF THE PSILOTACEAE, THE EQUISETACEAE AND THE LYCOPODIACEAE WITH NOTES ON THE DISTRIBUTION OF THE SPECIES

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(With 4 Plates and 3 figures in the Text.)

CONTENTS

PAGE.

I. INTRODUCTORY 62

II. DESCRIPTIVE 63

A. Psilotaceæ 63

B. Equisetaceæ 65

C. Lycopodiaceæ 68

III. SUMMARY AND GENERAL REMARKS 71

IV. ACKNOWLEDGMENTS 73

V. BIBLIOGRAPHY 73

I.—INTRODUCTION.

Flowering plants of the Bombay Presidency are well worked out through the successive efforts of Dalzell and Gibson (1896), Woodrow (1900), Gammie (1903), Cooke (1908), Talbot (1909), Bhide, Saxton and Sedgwick (1918), Blatter and McCann (1928) and many others ; but the cryptogamic plants with the exception of ferns worked out by Macpherson (1894), Blatter (1908), Blatter and d'Almeida (1922), remained almost unstudied. I, therefore, at the kind suggestion of Prof. D. L. Dixit undertook in 1932 a study of the cryptogamic flora of the Bombay Presidency with special reference to the vascular cryptogams. Since then I have been searching for the cryptogamic plants all over the Presidency (excluding Cutch, Kathiawar and Sind) and the adjoining districts of the Mysore State which forms a part of the same botanical province. I propose to put together in these studies, the data I have gathered during the last six years, regarding the occurrence, habit, distribution and ecology of the various species I have studied.

While collecting the species in field, it had been my special endeavour to study the surroundings in which the species occurred, as I believed that we knew so little about the sociology of the vascular cryptogams. I have recorded many new localities also, mainly based on my own observations and those of my colleagues Messrs[1] U. K. Kanitkar, B.A., M.SC., G. S. Deshpande, B.SC., B.T. and V. G. Bavadekar, B.SC. I have consulted many workers on the cryptogams in India, published literature on the subject as was available to me, and the herbaria of the College of Agriculture, Poona, Fergusson College, Poona, Bombay Natural History Society, Bombay, Gujarat College, Ahmedabad, and the Royal Botanic Gardens, Calcutta. A part of the information embodied in this paper is derived from them.

Now, regarding the plan of the present work, the part I of these studies deals with three families, the Psilotaceae, the Equisetaceae and the Lycopodiaceae; the part II deals with the Ophioglossaceae; a third and a fourth part will appear later, and they will deal with the remaining families. The full discussion of the observations made and the results obtained has been deferred till the last paper of the present studies, although some important points pertaining to certain species have been briefly considered here.

II.—DESCRIPTIVE.

A. Psilotaceae.

The family comprises two genera, *Psilotum* Sw. and *Tmesipteris Berhn.* The latter is an Australasian genus; only the former occurs in India. It has two species, viz. *P. triquetrum* Sw. and *P. flaccidum* Wall. *P. flaccidum* is common in Malaya but as yet it is not reported from any part of our Presidency or as a matter of fact from any part of British India. It is found in Mascarene Islands to the West and in Malaya Peninsula to the East of the Peninsular India. I, therefore, believe along with Raizàda (1935), that the species may be found in forests of the Peninsular India. But so far as the present investigations go, the only species I have met in our Presidency is *P. triquetrum*.

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[1] I take this opportunity to thank all these gentlemen for the help they rendered in course of this investigation.—T. S. MAHABALE.

PSILOTUM TRIQUETRUM SWARTZ.

(Plate I. figure 1.)

Diagnosis: Baker, p. 30. Clarke, p. 589.

Occurrence and habit.

The species occurs in limited areas in forests of the Western Ghats. It grows usually as an epiphyte on the rotten bark of trees in the forests in Shimoga district (Mysore State), or amongst the masses of aerial roots of coco-nut palms at Savantwadi (Bombay Presidency). It is not, however, unusual to find it growing terrestrially in crevices of moist rocks, looking down upon the mighty vistas of deep valleys in North Kanara. Thus for example, on a botanical excursion in company with Prof. V. V. Apte, the species was found to grow on cuttings of some rocks about two miles to the South of Karanzol Station on the Portuguese West Indian Railway (North Kanara). The surroundings of the species in this locality are typical enough for the species and deserve to be put on record.

The locality is a cool shady place in ever-green forest near Karanzol, not very far from Castle Rock (North Kanara). In the vicinity of the place grow lofty tree-ferns, *Alsophila latebrosa* Hook, and *Cyathea spinulosa* Wall, and a dwarf tree-fern, *Blechnum orientale* L. Deep *nallas* abound in the region; their precipitous walls are the favourite haunts of *Angiopleris evecta* Hoff. and beautiful Lygodias, *L. flexuosum* Bedd. and *L. microphyllum* R. Br. *Gleichenia linearis* Bedd., *Pteris pellucida* Presl., *Stenoloma chinensis* Bedd., and *Schizoloma ensifolia* J. Sm. make their appearance here and there but the most conspicuous fern in the immediate vicinity of *Psilotum triquetrum* is *Gymnopteris subcrenata* Bedd. From amongst the flowering plants in the neighbourhood, *Calamus rotang*, *Caryota urens*, *Terminalia paniculata*, *Lagerstromia lanceolata*, *Acacia concinna* are noteworthy. There is hardly a rock here which is not covered by moss, Jungermanniales e.g. *Lejeunea*, and grass. Small rivulets run down the rocks incessantly and maintain moisture in the surrounding air constantly, and favour thereby superabundance of cryptogams in the locality. The whole locality in fact, is highly suggestive of an aspect of a forest in some by-gone ages. But such ideal conditions are not obtainable everywhere in the Ghats and, therefore, the species shows a discontinuous distribution.

Distribution : shown in Text-fig. 1.

Savantwadi,[1] 'deeply embedded amongst the roots of coco-nut palm.'

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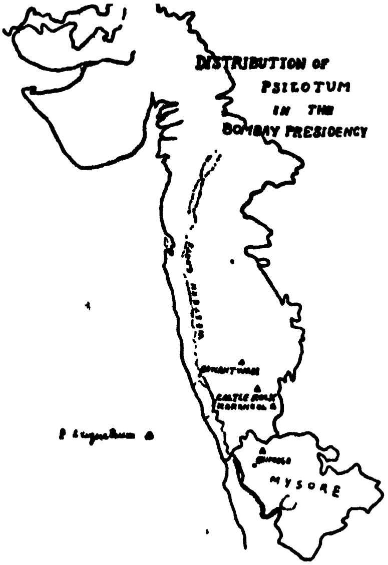
[1] Dalgado (1882), p. 544.

Castle Rock[1] (North Kanara), 'on moist rocks by the railway line, in ever-green forest, six miles to the North-West of the railway station.'

Karanzol[2] (North Kanara), 'in the crevices of rocks by the railway line, two miles due South of the railway station.'



TEXT-FIG. 1.—Map showing the distribution of the genus *Psilotum* in the Bombay Presidency.

B. *Equisetaceae.*

The family consists of a single living genus, *Equisetum* with about twenty to thirty species spread all over the world. According to Clarke (1880) the following four species occur in India :—

1. *E. arvense* Linn.
2. *E. diffusum* Don. Prodr.
3. *E. elongatum* Willd.
4. *E. debile* Roxb.

E. elongatum and *E. debile* belong to subgenus *Hippochaete* of Baker and are supposed to be more primitive than the species belonging to other subgenus *Equisetum proper*. *E. arvense* and *E. diffusum* belong to the latter sub-genus. In their distribution the first three species are more or less restricted to the Himalayan regions[1] while the last named species is spread throughout Northern India,[2] Punjab,[3] Bengal,[4] and the plains of Peninsular India.[4] So far as my present investigations go, the only species found at various places in the Presidency is *E. debile*. A distinct variety of this species is quite rampant in the bed of the river at Pashan, a village four miles to the North-West of Poona. This plant was first observed in this locality by Prof. R. K. Bhide—then of the College of Agriculture, Poona, in 1904. He simply named it as '*Equisetum* from Pashan.' Diagnosis of this new variety is given in detail here.

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[1] Mahabale, T. S., Sathe, G. S. and Apte, V. V., December, 1935.

[2] Mahabale, T. S., October, 1936.

Equisetum debile Roxburgh.

Diagnosis : Baker, p. 5 ; Clarke, p. 594 ; Roxburgh, p. 745.

Occurrence and habit.

The species occurs all over the Presidency and seems to have a great tolerance for varied climates. It grows by the rivers either on sandy banks or in the ditches near-about. It thrives well in marshy places where water is not stagnant. It is usually associated with *Anuera indica, Riccia sanguinea, Ammania baccifera, Polygonum glabrum, Typha aungusti-folia, Cyperus esculentus, Eragrostis cynosucoides, Fimbrystylis complanata* and *Saccharum spontanum. Eragrostis cynosucides, Cyperus esculentus* and *Typha aungustifolia* often conceal the identity of the plant in its natural suuroundings. At Kopargaon the species was noticed to grow on the banks of the Godavari River to a height of eight to ten feet. The species is usually found on the plains although it is not rare in the hilly up-country also.

Equisetum debile Roxburgh, var. *pashan* Bhide (var. nov.).

(Plate II. Fig. 2.)

Diagnosis : plants smaller than *E. debile* proper, 20-100 cm. long, ¼-½ cm. broad, with 9 grooves on the stem, sterile branches few and irregular, arising usually from above the middle, fertile branches 2-3 below the terminal cone ; these also bear cones sometimes ; cones ovate, ovate-cylindrical, sometimes fusiform, mucronate and with short stalks.

It will be realised from the above description by those that are familiar with the classification of the species of *Equisetum*, that the differences shown by the plant from *E. debile* proper are suffi-

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1. Baker (1887), p. 1.
2. Clarke (1880), pp. 594-595.
3. Stewart (1869).
4. Baker (1887) ; Clarke (1880) ; Roxburgh (1874),

cient to warrant its separate existence as a distinct variety if not a species. Accordingly it has been separated and called

Equisetum debile Roxb., var. *pashan* Bhide.[1] (var. nov.).

Occurrence and habit.

The species grows at Pashan (Dist. Poona), on the banks of the Ram River. It survives even in places likely to be left dry in summer.

Distribution : shown in Text-fig. 2.

E. debile.

Kopargaon[2] (Dist. Ahmednagar), 'on the banks of the Godavari River.'

Pandharpur[3] (Dist. Sholapur), 'on the banks of the Bhima River.'

Wai[4] (Dist. Satara.), 'on the banks of the Krishna River.'

Tumuri[5] (Dist. Belgaum.).

Gokak[6] (Dist. Belgaum.), 'On the banks of the Ghataprabha River.'

Malsar[7] (Baroda State.), 'on the banks of the Narbada.'

Raisan[8] (Dist. Ahmedabad.) 'On the banks of the Sabarmati River.'

E. debile, var. *pashan.*

Pashan[9] (Dist. Poona), 'abundant near the dam in the Ram River.'

Poona,[10] 'on the banks of the Mutha River.'

Vitthawadi[11] (Dist. Poona.), 'along the banks and in the river-bed of the Mutha River;' 'at various places upto Khadakvasala.'

Aundh[12] (Dist. Poona), 'on the banks of the Mula River.'

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[1] Following the international rules of botanical nomenclature I have associated this variety with the name of Prof. Bhide who was the first to observe it at Pashan, as far back as 1904.

[2] Mahabale, June, 1932.

[3] Phatak, V. G. (1935), p. 12.

[4] Prof. D. L. Dixit.

[5] Herb. Agri. College, Poona.

[6] Herb. Agri. College, Poona (Talbot's collection).

[7] Dixit, S. C.

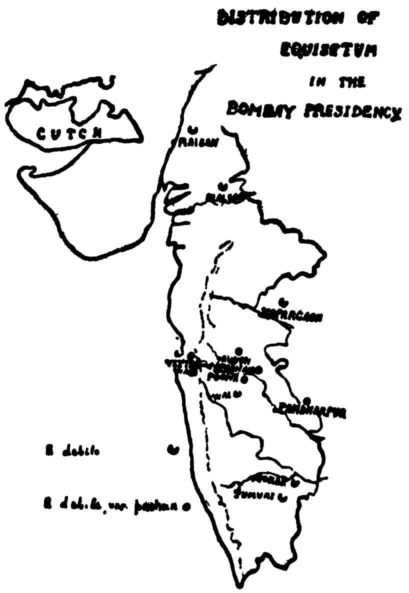
[8] Saxton (1918), p. 323. Herb. Gujarat College, Ahmedabad.

[9] Prof. R. K. Bhide, 1904 ; Herb. Agri. College, Poona.

[10] Mahabale, 1934.

[11] Deshpande, G. S. and Bavadekar, V. G., November, 1935.

[12] Prof. S. V. Shevade.



TEXT-FIG. 2.—Map showing the distribution of the genus *Equisetum* in the Bombay Presidency.

C. *Lycopodiaceae.*

The family comprises two homosporic genera, *Lycopodium* L. and *Phylloglossum* Kunze, and two heterosporic genera, *Selaginella* (R. B.) Spring and *Isoetes* Linn. Only the homosporic genera are considered here.

Phylloglossum is a monotypic genus found in Tasmania, West Australia, Victoria and New Zealand.[1] *Lycopodium* on the other hand is spread all over the globe and has about 94 species.[2] According to Chowdhury (1937) there are about 32 species of *Lycopodium* in India. The following six species are reported from the Bombay Presidency :—

1. *L. Hamiltonii* Spring.
2. *L. petiolatum* Herter.
3. *L. phlegmaria* L.
4. *L. cernuum* L.
5. *L. imbricatum* (?).[3]
6. *L. obtusatum* Fairbank. (? *L. obtusifolium* Hamilt. ?).[3]

[1] Baker (1887), p. 7.

[2] Baker (1887).

[3] These two species are not mentioned by Chowdhury (1937). They are included here on the authority of Birdwood (1891). Similarly L. phlegmaria is included here on the authority of Blatter (Natural Orders, p. 20).

I have not been able to examine the material of *L. petiolatum*, *L. phlegmaria*, *L. imbricatum* and *L. obtusatum* from our Presidency. My study is, therefore, limited to two species only, viz. *L. Hamiltonii* and *L. cernuum*.

Lycopodium Hamiltonii Spring.

(Plate III, Fig. 3.)

Diagnosis : Baker, p. 10 ; Clarke, p. 590 ; Spring, part I, p. 35.

Occurrence and habit.

The species is found growing at the forking of trees like *Pieris ovalifolia* in damp shady ravines.[1] It can be had in fair amount in the upper part of the Darjeeling[1] district and adjoining Sikkim (below Yoksam, for instance) and is reported from the Sarju valley, the Nilgiris and others parts of India.[2] The only authentic specimens of this species from our Presidency examined by me, were from Talbot's collection in the herbarium of the College of Agriculture, Poona. They were collected at Ainsi (North Kanara). I have compared these specimens with many other specimens of the same species obtained from different parts of India, and I find that they conform more to the specimen sent to me by Prof. H. G. Champion, M.A., from Lohajang, Kailganga V, Garwal (Kumaun Himalayas), rather than to the specimens collected at Mawphlong (Assam) by Prof. S. P. Agharkar, M.A., PH.D., Calcutta. Plate III, Fig. 3 is given here to give an idea of the habit of the plant, so that those that are more favourably placed than myself might collect it from some part of North Kanara.

Lycopodium cernuum L.

(Plate IV, Fig. 4.)

Diagnosis : Baker, p. 23 ; Clarke, p. 591 ; Spring, part I, p. 79.

Occurrence and habit.

The species is fairly common at Castle Rock, Karanzol, Collem and hills in the neighbourhood in the Goa Territory. It is much more so to the South of this region in the district of South Kanara. Formerly the species was available locally in Bangalore also, but owing to the frequent disturbance by the cow-boys, who used this locality as a pasture ground for cattle, the species has been now extirpated.

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[1] Prof. H. G. Champion's letter to the author, dated 13th November, 1937.

[2] Mr. V. Narayanaswami's letter to the author dated 15th November, 1937.

The species is found in what may be called *Gleichenia*—*Blechnum* association in North Kanara. At Bangalore also, it was associated with *Gleichenia linearis*. In some parts of North Kanara forests, it grows luxuriantly and the looping stem may reach a length of 10 feet or more. Comparatively small shoots come up vertically from this stem and bear the cones (Pl. IV, Fig. 4). They also reach a height of three to four feet. Vegetative reproduction is the principal mode of reproduction and large thickets are formed thereby. I know a hill near Castle Rock which is entirely covered by this lycopod. The normal habit of the plant is creeping and not erect as Pritzel[1] describes and figures it. I entirely agree in this respect with the remarks made by Holloway[2] and Chowdhury[3] about Pritzel's wrong account of this species. The creeping stem arches like a stolon, roots at the tip, and sends up the vertical branches; they bear numerous strobili (Fig. 4, pl. IV).

The species is limited in its distribution—so far as Bombay Presidency is concerned, to North Kanara forests; and even there it hardly crosses the limits of its present habitat.

Distribution : shown in Text-fig. 3.

L. Hamiltonii.

Ainsi[4] (North Kanara).

Konkan.[5]

L. Phlegmaria.

North Kanara.[6]

Konkan.[7]

L. Phlegmaria.

South Konkan,[8] 'parasitic, pendulous.'

L. Cernuum.

Castle Rock[9] (North Kanara), '*Chalk*[10] *Hill* on the railway line, two miles to the North of the railway station."

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[1] Pritzel (1902), p. 603, Fig. 379 (in Die Naturlichen Pflanzenfamilien, Tiel I Ab. IV).

[2] Holloway (1916), pp. 255-256.

[3] Chowdhury (1937), p. 201.

[4] Herb. Agri. College (Talbot's collection), Poona.

[5] Baker, p. 10; Kew Herb.

[6] Kew Herb.

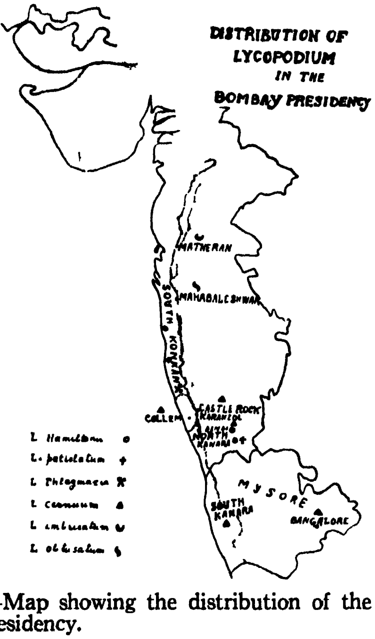
[7] Baker, p. 10.

[8] Blatter (1922-23). Natural Orders, p. 20. Devimani, McCann. The locality requires reconfirmation.

[9] Herb. Agri. College, Poona; Herb. Gujarat College, Ahmedabad; Mahabale, 1934.

[10] This hill is wrongly named so. There is no 'chalk' as is known to geologists. It is full of clay derived from the decomposition of granite containing kaolin.

'Hill[1] opposite the Chief Excise Officer's bungalow, three furlongs to the North of the railway station.'
Karanzol[2] (North Kanara), 'on the cutting of kaolin quarries.'
Collem[3] (Goa Territory), 'on the hills.'
South Kanara.[4]
Bangalore[5] (Mysore State), 'near Malayeshwaram.'
L. imbricatum (?).
Matheran,[6] 'in damp shady places.'
L. obtusatum Fairbank (?-*L. obtusifolium Hamilt.* ?).
Mahableshwar,[7] 'Fitzgerald Ghat.'[8]



TEXT-FIG. 3.—Map showing the distribution of the genus *Lycopodium* in the Bombay Presidency.

III.—SUMMARY AND GENERAL REMARKS

The foregoing pages give an account of the occurrence, habit, ecology and distribution of *P. triquetrum, E. debile, E. Debile, var.*

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1. Mahabale, October, 1935.
2. Mahabale (1937), p. 145.
3. Herb. Agri. College, Poona; Herb. Gujarat College, Ahmedabad.
4. Prof. L. Narayana Rao, Bangalore; Cal. Herb. (?).
5. Dr. M. A. Sampathkumaran, Bangalore.
6. Birdwood (1890), p. 211.
7. Birdwood (1891), p. 107.
8. This locality was once mentioned to Prof. V. V. Apte, Poona by Father Blatter in 1931. Further confirmation is desirable.

pashan and six species of Lycopodium found in the Bombay Presidency. The paper makes no pretence to be exhaustive but presents only a summary of the observations made by the author on vascular cryptogams during past six years.

Finding of *P. triquetrum* in the Presidency is of great interest as the Psilotales[1] are believed to be the most primitive vascular plants living today. The species is limited in its distribution to that great plexus of North Kanara forests which stand on the solid block of the Archean rocks—the granites and gneissess.[2] The vegetation in these forests has, *inter alia,* preserved some archaic features even to this date—as can be inferred from the occurrence of tree-ferns, lycopods, and numerous species of ferns. Of ferns Blatter[3] remarks, 'as a matter of fact three-fourths of all the species known in the Presidency have been found in North Kanara.' The presence of *Psilotum* in these forests, therefore, is not merely a matter of chance. To me it appears more to be the result of the geological history of the place, than merely an effect of the climatological conditions, prevalent in that part of the Presidency.

Equisetum debile is fairly common on the plains of the Presidency, along the banks of rivers taking their origin in the mountainous chain of the Western Ghats, and running down to the plains.[4] Roughly speaking, the genus appears to have spread from its head-quarters in the Ghats to the plains along many divergent lines—represented by rivers on the map given in the Text-fig. 2.

The genus *Lycopodium* includes three epiphytic species, *L. Hamiltonii, L. petiolatum*—both belonging to *Selago* group and *L. phlegmaria*—belonging to *Phlegmaria* group, one terrestrial species, *L. cernuum*—belonging to *Cernua* group, and two other species of unknown identity. *L. cernuum* seems to grow well in the Presidency, as the length reached by individual plants is ten feet or more, and hence certainly comparable to the length attained by individual plants in New Zealand. Holloway[5] (1916) says that in North Auckland individual plants of L. *cernuum* attain to a length of 12-15 feet. Here in the Bombay Presidency the maximum length attained by individual plants is ten feet. But still it is considerable for the conditions under which the species grows. The species, therefore, must be considered as one of the largest living lycopods in India. Like ***Psilotum triquetrum*** it is restricted in its distribution to certain places only, viz., Castle Rock. It is not yet reported from other places in the Presidency which have the same amount of rainfall and temperature. It grows, however, in plenty to the South of this region in South Kanara, and in the Nilgiris.[1] Evidently the species appears to have reached its extreme northern limit in the Western Ghats in that district. Its localised condition in North Kanara and disjunction in distribution beyond that part in the Presidency must be considered as due to historical reasons rather than to the stress of the climatological conditions. If this be really so, the places where the species occurs at present in the Presidency, will have to be considered as refuges of the modernised relics of the Palaeozoic lycopods.

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[1] Bower (1935).

[2] Wadia (1919) ; *Bombay Gazetteer.*

[3] Blatter (1908), p. 599.

[4] This statement excludes the consideration of *Equisetum* found in Cutch and Gujarat. It is of an altogether different origin there, and I hope to discuss this point in my subsequent paper.

[5] Holloway (1916), pp. 255-256.

IV.—ACKNOWLEDGMENTS.

I have to thank Prof. D. L. Dixit for suggesting me the problem, to Profs. S. P. Agharkar, M.A., Ph.D. and H. G. Champion, M.A., F.N.I. for the specimens of Himalayan lycopods they kindly sent to me, to Mr. V. Narayanswami, M.A., for identifying the species for me and giving me the necessary information from the Herbarium of the Royal Botanic Gardens, Calcutta. I have also to thank Dr. M. A. Sampathkumaran, M.A., Ph.D., and Prof. L. Narayan Rao, M.Sc., F.R.M.S. for their sympathy and help, and for the information they gave regarding *L. cernuum* and *P. triquetrum*.

My best thanks are due to the authorities of the herbaria of Agricultural College, Poona, Royal Botanic Gardens, Calcutta and the Bombay Natural History Society. The photographs in plates I, II, III and IV were taken by my colleague Mr. R. J. Kharadi, B.SC., and I am indebted to him for them.

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[1] For the full distribution of this species in India see Chowdhury (1937), pp. 194-195.

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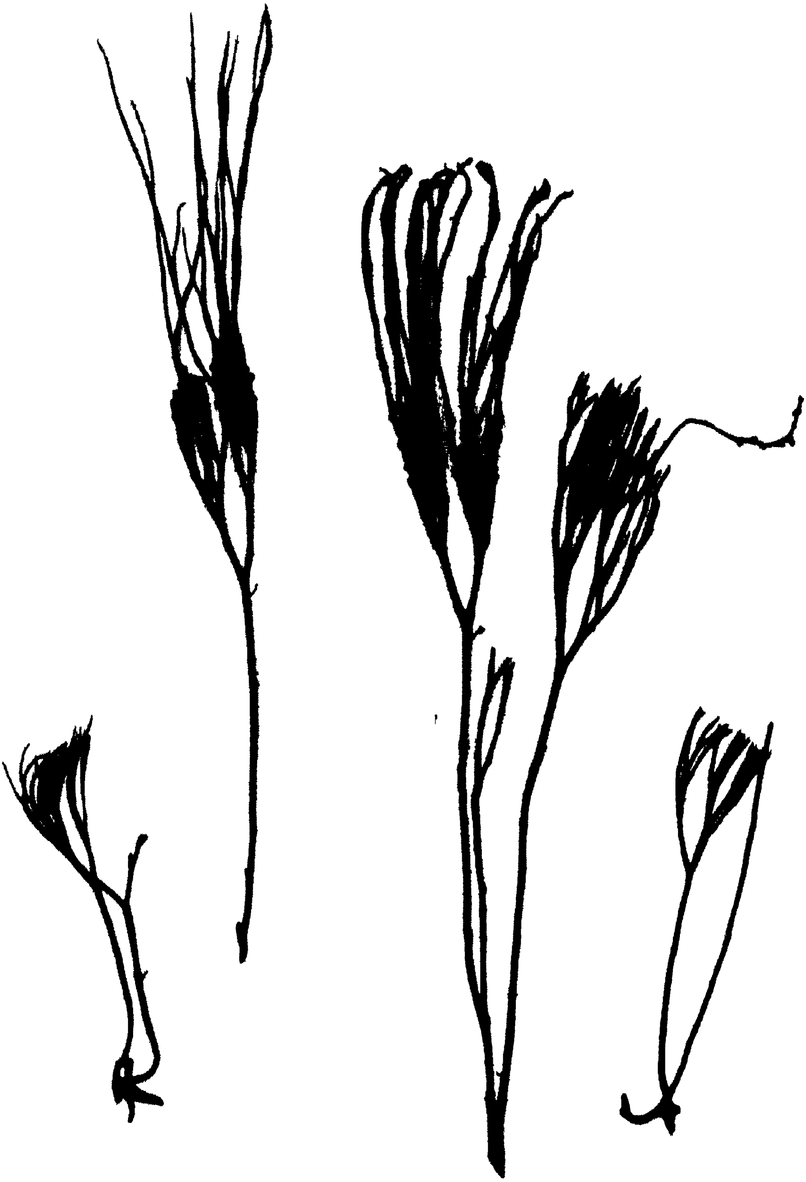

PLATE I. FIG. 1. *Psilotum triquetrum* Sw collected at Castle Rock (North Kanara). ½ Natural size.

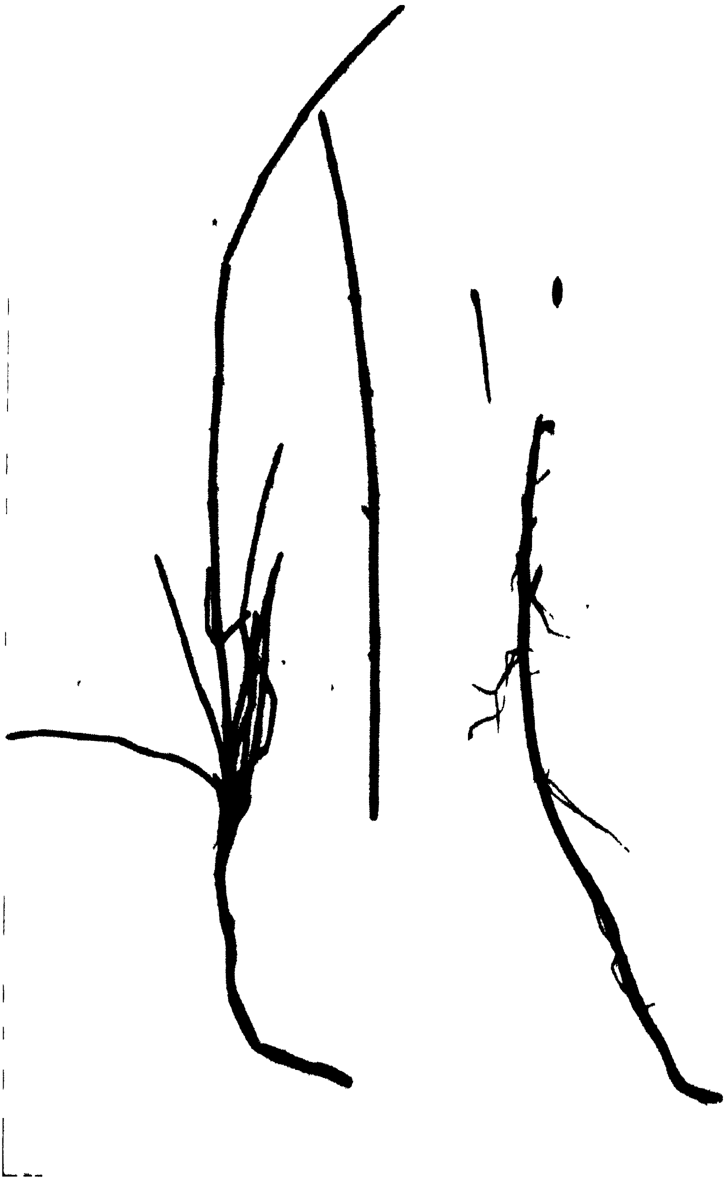

PLATE II FIG 2 *Equisetum debile* Roxb var *pashan* Bhide collected at Pashan (Dist. Poona). $^1/_3$ Natural size.

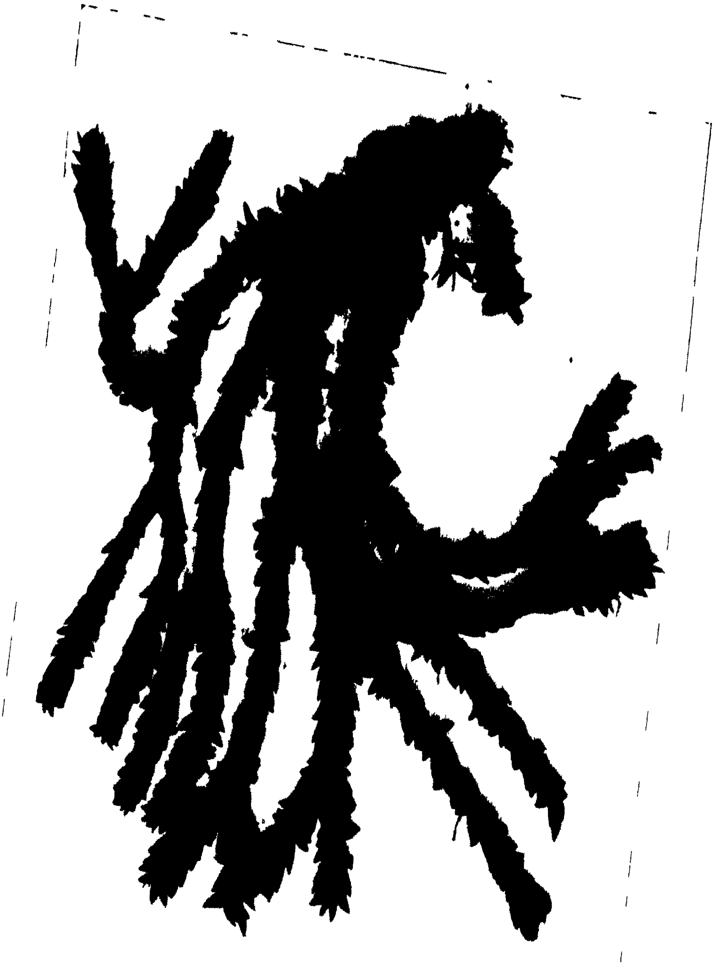

PLATE III FIG 3 *Lycopodium Hamiltonii* Spring Note the pendulous habit of the plant. 1/3 Natural size

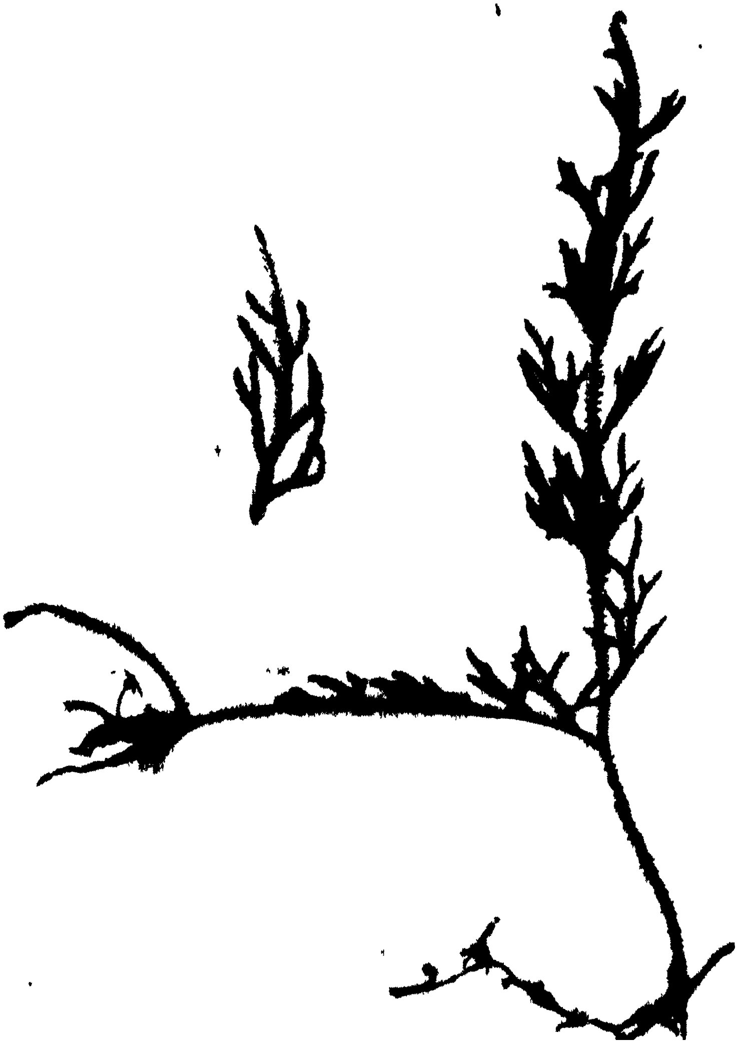

PLATE IV FIG 4. *Lycopodium cernuum* L collected at Castle Rock (North Kanara) (Much reduced). Note the creeping habit of the plant. The erect shoots bearing numerous sporangia sprout up from the tip of the creeping stem. The upper figure to the left shows the terminal portion of a storbiliferous branch with many cones.

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THE SKELETON OF PERIOPHTHALMUS BARBARUS (LINN.)

(1) THE SKULL

(*With 1 text and 5 plate figures.*)

By

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PREPARATION OF THE SKELETON.

As the fish is very small, the method of clearing it ' in toto ' was found to be satisfactory for studying its skeletal elements ' in situ '. Accordingly specimens preserved in 70% alcohol, were first washed in running water for about 5 hours and then put into 1% solution of sodium hydroxide for 25 days with three or four changes. In order to decolourise the pigments the specimens were exposed to the sun's rays for about 4 hours daily during this period. Approximately at the end of this period, the skin and the flesh were rendered transparent and through them the skeletal parts in their natural position were clearly seen in bright light. After this the specimens were preserved in glycerine with a crystal of thymol. If the specimens were kept further in the sodium hydroxide solution the soft parts were dissolved and the skeletal parts got disarticulated.

As recommended by Gloria Hollister[9] the specimens cleared as above were kept in alizerine dye till the skeletal parts were well stained. Although she got good results by this method, no differentiation was obtained in the staining of the soft and hard parts of this fish. The skeleton ' in situ ' was therefore studied without staining.

To disarticulate the skull a 10% solution of sodium hydroxide was used. On slightly heating this solution all the bones separated out easily.

The skeleton of this fish will be described in two parts, the first of which deals with the skull.

THE GENERAL CHARACTERS OF THE SKULL

There are extraordinary specializations in the skulls of these mud-skippers and various ichthyologists[8] have given a special name to these types of skulls as "Goby types". There are very large orbits (fig. 1 and plates 4 & 5) which are lifted above the rest of the skull and the eyes are very prominent and erectile. The quadrate—articular joint (fig. 1) is moved forward in front of the orbital rim. The jaws are of modified nipping type with remarkably stout protrusible premaxillæ, reduced maxillæ and interlocking maxillary processes of the palatines.

The hyomandibular (fig. 1 & plate 3) is remarkably wide anteroposteriorly. On the lower end of this bone, the preopercular appears as an almost vestigial patch. The inter-opercular forms the tracker that is characteristic of advanced derivatives of the Percomorph stock. The post-temporal is, however, not remarkably large, and has but a small contact with the stout occiput. The parietals, the mesopterygoids and the nasals are totally absent. The absence of the mesopterygoid led to a great confusion in naming the bones. The symplectic which corresponds in position to the metapterygoid was mistaken to be the metapterygoid and the metapterygoid itself to be the mesopterygoid. But taking into consideration their relation with the hyomandibular and quadrate, Tate Regan[15] has corrected their nomenclature. Similarly the absence of the parietals is very likely to mislead a beginner because the epiotic on each side (fig. 1) appears to be divided into two parts due to an outpushing formed by the groove for the posterior semicircular canal on the cranial side of this bone. The portion of the bone in front of this outpushing was taken by Emery[6] to be the parietal, and the portion behind the outpushing as the epiotic proper. But close observations show that the bone in question is not at all divisible and the entire bone is the proper epiotic.

As in other fishes the skull of this fish (fig. 1) is composed of the cranium, the sense capsules, and the visceral skeleton. The first two of these are fused together and form a compact structure. For descriptive purposes, we may call this fused, compact structure as the cranium; that is, this fused structure means the skull minus the visceral skeleton. The cranium (fig. 1 and plates 4 & 5) is a rounded, flattened structure and is produced anteriorly into a straight ventral and a curved dorsal bony bar. Posteriorly it narrows towards the occiput which projects behind, and provides articulation for the vertebral column. From the occiput the dorsal surface of the cranium (plate 4) slopes upwards to its anterior margin. From the median line, it slopes down symmetrically towards its left and right sides. In its posterior half, it bears a small triangular, median, vertical plate which is more prominent in other fishes. Its antero-lateral corners are produced into stout downward processes (V. Pr.) and from the middle of its anterior edge a bony bar (Fr. B.) curving over and between the eye-sockets, meets the bony wall of the ethmoidal region which serves as the anterior border of the orbits.

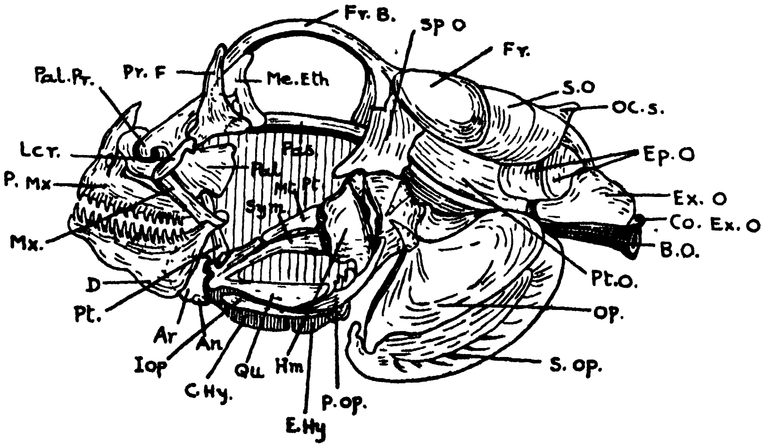
The ventral surface of the cranium (plate 5) is nearly flat. The median stout and straight bony bar projecting forward from its anterior edge, thickens and broadens out anteriorly in front of the eye-balls. Both the internal and external surfaces of the cranium are uneven and irregular and are cut up into irregular areas according to the forms and outlines of its component bones.

The cranial chamber is big and elongated. Its roof (plate 4) is mainly formed by the frontal (Fr.) supra-occipital (S.O.) and even the ex-occipitals (Ex. O.), which meet in the mid-dorsal line of the cranium and take part in covering the posterior part of the brain from the dorsal side. The parasphenoid (plate 5, Pa. S.) and the basioccipital (B.O.) form its floor. The sense capsules are well developed except the nasal. The eyes are very prominent, large in size and situated very close together. Each orbit (plates 1 and 4) is bounded anteriorly by the prefrontals (Pr. F.), laterally on the inner side by the frontal bar (Fr. B.) and posteriorly by the frontal (Fr.), alisphenoid (Al. sph.) and sphenotic (Sp.O.). The ring of bones generally found on the dorsal side is totally absent. The foramen for the optic nerves is formed in between the spur-like processes (plate 2, spu.) of the parasphenoid. The latter like the frontal has got a long anterior prolongation just below the frontal bar and is attached to the vomer and mesethmoid in the ethmoidal region. Posteriorly its conical part is embraced by the basioccipital between its two arms (plates 2 & 5).

The cranium is divisible into the occipital region and the otic capsules behind, the frontal region in the middle and the orbital and ethmoidal regions in front. The occipital region is narrow behind but broadens out anteriorly. It is bounded by the basioccipital ventrally (plates 2 & 5, B.O.) and by the ex-occipital (plates 1, 2, 4 & 5; Ex. O.) dorsally and laterally, and by the supra-occipital (plates 1 and 4, S. O.) dorsally in front. This occipital region is continued ahead without any partition into the otic and the frontal regions, the former occupying the sides, and the latter the middle portion of the cranium. There is no bony partition between the frontal region and the otic region. The latter is well developed and all the otic bones appear to be present. It can be said in general that of these bones, the epiotics (fig. 1 and plates 1, 2 and 4, Ep.O.) the pterotics (Pt.O.) and the sphenotics (Sp.O.) are on the dorsal side and the pro-otics (Pr.O.) and ophisthotics (Op.O.)

on the ventral side. To be exact, the epiotic is strictly on the dorsal side, while the pterotic is on the dorsal as well as on the lateral and ventral sides of the otic region. Similarly the sphenotics are situated on the dorsal as well as on the antero-lateral and ventral sides of the cranium and they are a little away from the auditory capsules, and do not take any part in the formation of the same, but serve to form the posterior border of the orbits. The pro-otics, the pterotics, and the sphenotics are relatively large bones, while the epiotics and the ophisthotics are small. All these bones except the sphenotics are found to accommodate the semi-circular canals into the grooves formed along their cranial surfaces facing one another. From the ventral side of the cranium, the prominent otolith is clearly seen through the fontanelle (plate 5, Fo.) situated in between the two arms of the ophisthotic.

The frontal region is bounded dorsally by the frontal (plate 1, Fr.) and ventrally by the parasphenoid (plate 5, Pa. S.) and its cavity is mostly occupied by the brain. These two bones are the largest bones of the skull and occupy most of the area in the mid-dorsal and mid-ventral regions of the cranium. Both the bones have got slender anterior prolongations which meet the mesethmoid in the ethmoidal region.



TEXT FIG. 1. Dorso-lateral view of the skull. × 12.
An. = Angular ; Ar. = Articular ; C. Hy. = Ceratohyal ;
Co. Ex. O. = Condyle of the Ex-occipital ; D. = Dentary ; E. Hy. = Epihyal
Hm. = Hyomandibular ; I. Op. = Inter-opercular ; Lcr. = Lachrymal ;
Mt. Pt. = Metapterygoid ; Mx. = Maxilla ; Op. = Opercular ;
Pal. = Palatine ; Pal. Pr. = Palatine process ; P. Mx. = Pre-maxilla ;
P. Op. = Pre-opercular ; Pt. = Pterygoid ; Qu. = Quadrate ;
S. Op. = Sub-opercular.
Remaining letters same as in Plates 4 and 5.

In front of the frontal region is the orbital region without any orbital septum in between the two eye-sockets. As mentioned above, each orbit is bounded anteriorly by the prefrontal and laterally on the inner side by the frontal bar and posteriorly by the frontal, alisphenoid and the sphenotic. The ventral process of the last bone forms the postero-lateral border on the external side of the orbit.

In front of the orbits is the ethmoidal region formed by the median single mesethmoid (fig. 1 and plate 1, Me. Eth.) which separates the nasal chambers from the orbital. The former in front of the ethmoidal bony wall are not bounded by any prominent bones.

The average adult skull measures about 1 centimetre while its breadth at its widest plane is only half a centimetre. Compared with the skull of a common bony fish like Sciænid it is rendered remarkable by the shortening of its pre-orbital portion (fig. 1) and by the dorsal bulge of the anterior frontal bar between the spacious optic cavities.

The bones of all these regions, viz., the occipital, the otic, the frontal, the orbital and the ethmoidal and also the visceral arches will be now dealt with in great details.

BONES OF THE OCCIPITAL REGION

(Fig. 1 and plates 1, 2, 4 and 5.)

The Exoccipital. The foramen magnum (Plate 4, F. M.) is mostly bounded by the two exoccipitals (Ex.O.) which dorsally meet over it and ventrally (Plate 5) articulate with the sides of the basioccipital. Their dorsal joint being long and straight pushes forward the supraoccipital (Plate 1, S. O.). Each of them (Plates 1, 2, 4 and 5, Ex. O.) is an irregular bone greatly resembling a half of a short flower vase. Posteriorly it has a rounded projection (Plate 1 Pr. Ex. O.) bearing a concave facet (Fa. Ex. O.) lined with cartilage for the corresponding facet on the atlas. As it anteriorly spreads outwards and upwards it encloses a large cavity. It has a vertical rod-like process (R. P.) which articulates ventrally with the median basioccipital. On the side it bears a large foramen for the exit of the tenth cranial nerve (Plates 2 and 5, F. X.). There is also another small foramen behind the first for the exit of the twelfth cranial nerve (Plates 2 and 5, F. XII). Anteriorly they are bounded by the median supraoccipital and the lateral epiotics. The bone is partly cartilaginous and partly ossified and bears ridges and depressions on its cerebral side.

The Basioccipital. (Fig. 1, & plates 2, 4 & 5). The median basioccipital (B.O.) forms the floor of the cranium in the occipital region and bears a concave occipital condyle posteriorly. It is a Y-shaped bone with a thick base and flattened branches. The laminar portion joining the two branches is well ossified. Its ventral surface is smooth and convex while its dorsal or cerebral surface has got a median groove and two lateral pockets into which fit the expanded ends of the rod-like cartilaginous processes of the ex-occipitals. Into the concavity between its two branches or arms fits the posterior conical end of the parasphenoid and to the two oblique and strengthening edges of the two arms are touching the pro-otic bones. Its lateral corners are covered by the ophisthotics.

THE SUPRAOCCIPITAL. (Fig. 1 & plates 1 & 4, S.O.). It is a thin characteristic rhomboid bone directed obliquely upwards and forwards from the foramen magnum, in bordering which it does not take any part. On the dorsal surface it is produced into a median triangular plate which is not very prominent on account of the oblique position of this bone. The dorsal edge of this plate is relatively very stout and is known as the occipital spine (Oc. S.), which is firmly embedded in the longitudinal muscles on its dorsal side, and thus helps to bind the vertebral column to the skull. This spiny process is supported by radiating ridges or laminar thickenings of the supraoccipital directed forwards. Except these ridges the bone is well ossified. Its cerebral side is concave. Its anterior apex fits into the corresponding groove in the posterior portion of the frontal, the laminar portion of which covers its lateral corners. The supraoccipital is surrounded anteriorly by the frontal and laterally by the epiotics which cover its sides. The ex-occipitals situated posteriorly also cover its basal portion.

BONES OF THE OTIC REGION

(Fig. 1 & plates 1, 2, 4 & 5.)

THE EPIOTIC. (Plate 1, Ep. O.). Anterior to the dorsal part of the ex-occipitals is a pair of bones—the epiotics. Each of them is polygonal and scale-like with a concave cerebral and a convex dorsal surface. Its surface is divided into outer and inner zones by a tunnel for the posterior semi-circular canal. It bears a triangular bony projection (Plate 1, Pl. A. Po. T.) in the middle of its outer side with which is articulated the upper arm of the post-temporal bone. It is well ossified throughout except for a narrow cartilaginous rim round the edges. The bone has got the frontal and the pterotic on its anterior side, the supra-occipital on its inner side and the ex-occipital behind.

THE PTEROTIC. (Fig. 1 & plates 1, 2, 4 & 5. Pt. O.). Just to the antero-lateral side of the epiotic is the longish pterotic bone consisting of two bony laminae and a bony ledge (B. L.) extending outside along its middle. Its dorsal lamina (Plate 1, D. L.) is broad and forms a large part of the roof of the cranium in the auditory region. Along the base of the ledge (Plate 1, B. L.) the bone is traversed by a tunnel for the external semi-circular canal. The ledge is supported by the ventral lamina, and its base is very much thickened. The bone is partly ossified and partly cartilaginous and bears a shallow concavity (Fig. 2, C. P.) for articulation with the posterior process of the hyomandibular. The bone is surrounded by the sphenotic, the frontal and the epiatic bone, the last two of these overlap its mesial side.

THE SPHENOTIC. (Fig. 1 & plates 1, 2, 4 & 5, Sp. O.). It is a deep-watch-glass-shaped bone forming the anterolateral corner of the brain-case. On its external surface, it has a narrow bony ledge which extends outwards along the anterior margin of the brain-case. The transverse part of this ledge is free from the base and extends obliquely inwards and forwards and joins the similar splint-like process of the frontal to form the posterior border of the orbit. It has also a pointed stout process directed obliquely downwards and outwards. This ventral process (V. Pr.) is not solid but consists of a thick bony lamina, folded like a leaf along the middle. Posteriorly at the base of this process there is a conical socket (Plate 5, C. A.) providing articulation for the anterior projection of the hyomandibular. The concave cerebral surface of the sphenotic is raised into ridges dividing its cavity into irregular pockets. Its thickened central part is partly cartilaginous and partly ossified while its peripheral laminar parts are completely ossified.

THE PRO-OTIC. (Plates 2 & 5, Pr. O.). Situated on the ventral side of the brain-case is the pro-otic—a flat, thick angle-like bone with its one long and broad arm extending obliquely backwards and inwards and articulating with the corresponding arm of the basi-occipital, and the other short and flattened arm extending upwards and covered by the parasphenoid forming the anterior wall of the brain-case. The two pro-otics enclose (Plate 5) between them a diamond shaped portion of the parasphenoid. The ventral surface of the pro-otic is relatively smooth and is pieced by a large foramen situated at the junction of its two arms and providing for the exit of the fifth and seventh cranial nerves (Plate 5, F. V.). In the middle of its inner margin there is another foramen (F. In. C.) which is open on the inner side in a disarticulated skull, but is surrounded by the parasphenoid in the entire skull. It provides for the entrance of the internal carotid artery. Its dorsal or inner surface is quite irregular and is supported by some equally irregular bony ridges. The basal and terminal portions of its arms are thickly cartilaginous.

The bone is surrounded by the parasphenoid, sphenotic, ophisthotic, basi-occipital and pterotic bones and is covered on its mesial side by the parasphenoid.

THE OPHISTHOTIC. (Plates 2 and 5, Op. O.). It is situated in front of the ex-occipital on the ventral side as a small, very thin and transparent bone. It is roughly triangular in outline, having a narrow outer arm resting on the pterotic and a broad inner arm covering some portion of the pro-otic and the basi-occipital. In front of this there is an oval fontanelle (Plate 5, Fo.) which is surrounded by the pro-otic and the pterotic in front, and by the two arms of the ophisthotic behind.

BONES OF THE FRONTAL REGION

(Fig. 1 and plates 1 and 5.)

THE FRONTAL. (Plate 1, Fr.). Situated on the dorsal side it is a large membrane bone covering nearly ¾th of the surface of the brain-case. Posteriorly it consists of two symmetrically rounded scale-like parts which are inseparably joined in the middle. Anteriorly it is made up of a bony compressed rod (Fr. B.) which curves up in the orbital region and bifurcates at its anterior end. Each of the flattened posterior parts of the bone, is produced into a broad bony plate along its lateral and posterior edges. In entire skull these plates cover the anterior curved portion of the supra-occipital and also the mesial parts of the sphenotic, pterotic and epiotic. Anteriorly it is produced into a dorsal plate, which along with the similar plate of the sphenotic forms the anterior border of the brain-case. Its cerebral side is concave and bears a prominent central ridge. Its anterior bifurcated portion is firmly attached to the dorsal side of the mesethmoid through an intervening cartilage. The whole bone is well ossified except the median ridge on its cerebral side. The bone is in contact with the sphenotic, pterotic, epiotic and supra-occipital in its posterior region, and with the mesethmoid and pre-frontals in the anterior region.

THE PARASPHENOID. (Fig. 1 and plates 2, 4 and 5. Pa. S.). The parasphenoid (Plate 2) is the longest bone of the skull extending from the basi-occipital to the vomer. In shape it is like a partly open lancelolate leaf with its tip directed backward, its anterior portion representing the petiole and the posterior corresponding to the blade or lamina. This lamina-like part forms the middle part of the floor of the brain-case and covers the mesial parts of the pro-otic and basi-occipital, and its petiole-like portion extends forward as a ventral bony bar in the inter-orbital region. Between the petiole and the lamina there is a transverse partition forming the anterior wall of the brain-case. It is produced into two lateral bony spurs (Spu.) which articulate along their external margins with the alisphenoids and enclose between themselves the foramen for the exit of the optic and the olfactory nerves. The petiole-like anterior part has a concave upper surface and further it contains a large cylindrical cavity which has a wide opening, as its anterior end is bevelled off. It is in this opening that fits well the base of the vertically situated mesethmoid. Seen from the ventral surface, the petiole is very much constricted into a vertical strengthening ridge immediately in front of its leaf-like portion. This is a well ossified characteristic membrane bone forming the ventral axis of the cranium. Its posterior conical end fits into the concavity formed between the two arms of the basi-occipital and its anterior end gives support ventrally to the vomer and dorsally to the mesethmoid. In the region of the brain case, it is surrounded by the basi-occipital, pro-otics, and alisphenoids, and in the ethmoidal region by the vomer and mesethmoid.

THE ALISPHENOID. (Plates 1 & 2. Al. Sph.). They are roughly triangular in outline and situated vertically forming the posterior wall of the orbits. They are held in position by the pro-otics, sphenotic, parasphenoid and frontal. It is attached to the spurlike process of the parasphenoid and is mostly cartilaginous and forms the anterior wall of the brain-case.

BONES OF THE ORBITAL REGION

In connection with this region very few bones are present. Generally in Teleosts a chain of bones is developed round the margin of the orbit but in this fish no such bones are found. As stated before, each orbit is bounded anteriorly by the prefrontal, laterally on the inner side by the frontal bar, and posteriorly by the frontal, alisphenoid and sphenotic. The ventral process of the sphenotic (Plate 4, V. Pr.) may also be mentioned here as forming the postero-lateral part on the external side of the orbit and may be looked upon as serving the purpose of the postorbital bones. The orbits are spacious and lifted above the rest of the skull. The interorbital septum is absent.

BONES OF THE ETHMOIDAL REGION

THE VOMER. (Plate 2, Vo.). The vomer forms the ventral axis of the cranium beyond the parasphenoid. It is a triangular bone with its anterior basal edge thickened to form a transverse partition between the orbital and the olfactory capsules. It gradually tapers posteriorly and supports the similar anterior end of the parasphenoid. Its ventral side is smooth while its dorsal side has got a ridge in the middle. The bone is well ossified except its basal portion which projects in front of the ethmoidal region, and which is fully cartilaginous.

THE MESETHMOID. (Fig. 1 & Plates 1 & 4, M. Eth.). The mesethmoid is a median unpaired bone forming the middle part of the bony wall between the orbitals and the nasal capsules. It extends vertically between the anterior end of the parasphenoid below, and that of the frontal above, and has got the form of a bony rod with a long, median and irregular thickening at the base, and two lateral flat processes above. Its basal part is pierced by a large aperture through which the olfactory nerves enter the nasal capsules. Its dorso-lateral processes extend outwards in front of the pre-frontals and support the similar processes of the bifurcated anterior end of the frontal bar. The mesethmoid with the pre-frontals attached to its sides looks like a butterfly (Plate 1) with its wings extended. Its thickened basal process fits into the hollow of the anterior end of the parasphenoid and bears on its sides articulating facets for articulating with the similar facets of the pre-frontals. The thickened portions of this bone are highly cartilaginous and the rest of the bone is well ossified.

THE PRE-FRONTALS. (Fig. 1 & Plates 1, 4 & 5, Pr. F.). The pre-frontals are triangular, membranous bones extending laterally on the sides of the mesethmoid. Each of them has at its ventro-median corner a short and thick process directed forwards and bearing the articulating facets. The mesial sides of these processes articulate with the lateral articular surfaces of the dilated ventral part of the mesethmoid. Similarly the dorsal part of the pre-frontal rests on the posterior surface of the dorsal processes of the mesethmoid. In this way two wide apertures are left between these three bones in the middle. These apertures (Plate 1, H. P.) are occupied by the posterior handles of the palatines. The upper laminar half of the pre-frontal appears to be formed of a row of flexible rays joined together by their sides. These rays appear to branch and increase in number distally. Some of them may be free at ends. On account of such peculiar formation of some of the bones of this fish, they have frayed edges and appear to end in soft fin-like portions. The ventro-lateral corner of this bone is thickened and provides articulation for the lachrymal (Lcr.). This is a well ossified bone except at its thickened corners and its dorsal fin-like part, which are cartilaginous.

THE NASALS. There is no trace of nasals in this fish.

THE LACHRYMALS. (Fig. 1 and Plate 1, Lcr.). From the ventro-lateral corner of the pre-frontal a thin-scale-like bone projects forwards and outwards to the maxilla. Its base bears a shallow pit covered with cartilage which loosely articulates with the cartilaginous portion of the pre-frontal. It is well ossified and lies on the outer side of the nasal chamber.

THE VISCERAL SKELETON

The remaining part of the skull consists of the various arches and opercular bones and they are described below under their respective heads :—

(i) THE PALATO-PTERYGOID BAR. (Fig. 1 and Plate 3). This arch serves as the support for the jaws. On each side it includes the palatine (Pal.), the two pterygoids (Pt. & Mt. Pt.) and the quadrate (Qu.). The latter is connected to the hyomandibular (Hm.) through a splint-like bone—the symplectic (Sym.). Generally in Teleosts there are three typical pterygoid bones (Ecto, ento and meso—pterygoids or they are also known as pterygoid, meso-pterygoid and meta-pterygoid respectively) but in this fish only two bones are developed and they too very much reduced and greatly modified.

THE PALATINE. (Fig. 1 and Plate 3, Pal.). The palatine has a form of an axe with its blade hanging down from its handle into the ethmoidal region. On each side the long part of the handle rests in the gap between the pre-frontal and the mesethmoid (Plate 1, H. P.) and the short anterior part rests in the hole (Plate 3, H. A. P.) in the head of the maxilla. Its blade is held in position between the edges of the broadened vomer and the anterior side of the pre-frontal. The blade is slightly curved and free ventrally, and it bears in the middle of its anterior edge a socket (So.) for articulation with the pterygoid. Its anterior edge and the dorsal part are thickened and the latter possesses on its inner side a socket for articulation with the vomer. It is a well ossified bone with cartilaginous patches at the ends of its handle and around the sockets.

THE PTERYGOID. (Fig. 1 & Plate 3, Pt.). This bone also known as the ecto-pterygoid, is a splint-like bone with an axial rod-like thickening extending between its two ends. Its narrow upper end fits into a socket present in the middle of the anterior edge of the palatine and its broad lower end is firmly attached to the base of the anterior side of the quadrate.

THE META-PTERYGOID. (Fig. 1 & Plate 3, Mt. Pt.). This is similar to the pterygoid but its bony support or rod-like thickening is along its anterior margin. This thickening becomes continued with the similar one on the anterior arm of the quadrate. The remaining part of this bone appears to be its plate-like expansion. Its upper broad end is attached to the hyomandibular through a thick band of cartilage. At its lower end its plate-like part articulates with a similar part of the anterior arm of the quadrate, but the axial rod of the former extends beyond this joint and fits into a groove along the anterior edge of the latter. It is a well ossified bone except at its ends which are cartilaginous.

THE QUADRATE. (Fig. 1 & Plate 3, Qu.). The quadrate is composed of two arms making an angle of about 70 degrees. Its anterior arm is short, narrow and directed obliquely upwards while the posterior one is long and broad, being directed horizontally backwards. Anteriorly at the junction of these arms there are two concavities separated by a curved condyle (Co.). This condyle and the concavities provide articulation for the lower jaw. On the inner side at this corner it is also provided with a rounded process which controls the movements of the articular bone. Posteriorly at the junction of its two arms it is provided with a small bony plate which is articulated with the lower end of the symplectic. The anterior arm of this bone is continued through the meta-pterygoid to the hyomandibular while its posterior arm ends freely and is loosely attached to the pre-opercular at its lower end. The bone is well ossified except at the articular sockets and condyles.

THE SYMPLECTIC. (Fig. 1 & Plate 3, Sym.). This splint-like bone is slightly curved and is supported by a thickening along its length. Along its anterior edge it is articulated with the meta-pterygoid and the anterior arm of the quadrate, thus strengthening the meta-pterygoid bar from behind. Its broad upper end articulates with the hyomandibular through a thick and broad cartilaginous band and its lower tapering end is firmly attached to a small projection of the quadrate in its angle. Like the previous three bones it is cartilaginous at its ends.

(ii) THE HYOMANDIBULAR. (Fig. 1 & Plate 3, Hm.). It is a rounded flat bone (Plate 3, Hm.) having an irregular outline and irregular surfaces. On its outer surface there project three radiating thickenings which broaden towards the margin and bulge out to form the condyles for articulation with the surrounding bones. It is provided with a bony ridge which descends across its outer surface, becomes free ventrally and projects below it. Along the posterior side of this ridge is attached the upper half of the pre-operculum. On its anterior side is a tubular foramen (F. Hm. N.) through which emerges the hyomandibular nerve. In front of this ridge, the lower half of the margin of this bone has got two shallow oval concavities for articulation with the metapterygoid and the symplectic as already observed. Of the three radiating thickenings two are directed obliquely upwards and the third backwards and downwards. The anterior-most condyle (S. Sp. O.) fits into the socket on the sphenotic and the middle one (C. Pt. O.) similarly articulates with the pterotic. Through the third condyle (C. Op.) the hyomandibular becomes articulated with the opercular bone (Op.). The inner surface of this bone is slightly concave and bears a short bony rod to whose end is attached the interhyal. The conical thickenings leading to the articular surfaces along the margin appear sometimes hollow, but usually they are plugged with cartilage. Thus with the hyomandibular five bones are articulated, viz., the metapterygoid, symplectic, interhyal, pre-operculum and operculum while the hyomandibular itself firmly hangs down from the cranium proper through two ball-and-socket joints.

(iii) THE UPPER JAW. (Fig. 1 & Plate 3). Each half of the upper jaw consists of two bones (1) the premaxilla and (2) the maxilla. Of these the former alone takes part in bounding the gape of the mouth and has a number of teeth.

THE PRE-MAXILLA. (Fig. 1 & Plate 3, P. Mx.). It is a thick curved bone consisting of two broad arms situated at right angle to each other. The ascending arms of the right and left pre-maxillæ come in close contact with each other by their inner edges. The horizontal arm of each has a broad and ventral edge and contains fourteen sockets for the lodgment of teeth (T. C.). This bone is irregularly thickened and ossified with the result that it appears to be made up of three pieces—one rod-like vertical, another teeth-bearing horizontal, and the remaining bent one, supporting and holding the previous two together. The vertical part of the third one is joined to the first one by a bony plate which has an aperture (F. Na.) between them, for the passage of the nasal artery. The jointed premaxillæ are movable up and down and are not articulated with any bone except the maxillæ whose heads provide a shallow groove on each side for the reception of the middle flat cartilaginous portion of the ascending arm of this bone. The bone is well ossified except the cartilaginous portion mentioned above and the similar one round about the sockets for the teeth.

THE MAXILLA. (Fig. 1 & Plate 3, Mx.). It is situated obliquely behind and between the dorsal end of the ascending arm and the outer end of the horizontal arm of the pre-maxilla, and extends beyond the latter. It is in the form of a curved blade with a perforated head into which fits the anterior end of the handle of the palatine. The head is, further, twisted so as to provide a shallow groove on its anterior face to support the vertical part of the middle bent piece of the pre-maxilla. The heads of the two maxillæ come close together (Mx.) and are joined behind the dorsal ends of the pre-maxillæ by a cartilaginous pad—the inter-maxillary cartilage which also connects them with the dorsal ends of the pre-maxillæ, and plays an important part in directing the movements of the jaws. Its lower shaft-like end partly rests on the posterior end of the horizontal arm of the pre-maxilla and extending beyond, rests, against the upper arm of the dentary. It is mostly ossified. This bone does not bear any teeth at all but only supports and facilitates the movements of the pre-maxilla and the dentary.

(iv) THE LOWER JAW. (Fig. 1 & Plate 3). Like the upper jaw, the lower jaw consists of two symmetrical halves which are united anteriorly by an intervening cartilage. Each half consists of the following bones :—

THE DENTARY. (Fig. 1 & Plate 3 D.). This is a thick, plate-like, strongly curved bone with a concave inner and convex outer faces, and borders the lower margin of the gape of mouth. Posteriorly it is produced into an oblique upward process which does not bear any teeth, and is supported externally by the lower end of the maxilla. Ventrally the process of the dentary is thinned out to a curved lamina and bears on its inner side a wide opening of a conical cavity extending into the bone anteriorly. This cavity receives the lower conical process of the articular bone. The upper edge of the horizontal part of the bone is broad, and contains a row of 14 sockets for the lodgment of the teeth. The bone is well ossified except its anterior end which is cartilaginous and through this it articulates with the fellow of the other side.

THE ARTICULAR. (Fig. 1 & Plate 3, Ar.). It is a flat, stout triangular bone with its anterior corner fitting into a similar cavity in the dentary. Its posterior side is produced in the middle into a curved process which provides a dorsal facet for the quadrate and a ventral one for the angular. The bone is well ossified and its articulating surfaces are coated with cartilage.

THE ANGULAR. (Fig. 1 & Plate 3, An.). It is a small roundish bone with an irregular outline. Anteriorly it has a condyle fitting into the ventral socket of the articular.

(v) THE HYOID ARCH. (Plate 3 & Fig. 1). The V-shaped hyoid arch is situated behind and inside the lower jaw and is connected with the skull through the hyomandibulars. It consis.s of two median bones and a row of 5 bones on each side.

THE UROHYAL. (Fig. 1 & Plate 3, Ur. Hy.). It is a median vertical bony plate connected anteriorly with the basi-hyal and hanging down in the middle between the hypo-hyals. It is further supported by being jointed to the lower pair of hypo-hyals and its free posterior end slightly supports the first basi-branchial. It is well ossified and is further strengthened by two radiating thickenings.

THE HYPO-HYAL. (Plate 3, H. Hy.). There are two hypo-hyals forming the anterior end of the hyoid bar on each side. The upper ones of these are triangular and plate-like with their anterior edges broadened, being turned inwards and approaching in the middle. The lower ones are also similarly bent and their posterior apices are lengthened. Both the lower and upper hypo-hyals are anteriorly thickened and cartilaginous while their posterior parts, thin but well ossified, are attached by their sides to the inner sides of the Cerato-hyals.

THE CERATO-HYAL. (Plate 3 & Fig. I, C. Hy.). This spoon-shaped bone is the strongest and the largest bone of the arch. Anteriorly the handle is flattened and broadened so as to provide a wide articular surface for the two hypo-hyals. The posterior part is thick and has a straight edge for articulating with the epihyal. The bone though thick and strong is mostly cartilaginous and poorly ossified.

THE EPIHYAL. (Fig. 1 and Plate 3, E.Hy.). The epihyal is a thick triangular bony plate articulating by its base to the similar edge of the ceratohyal and tapering posteriorly to its joint to the interhyal. At the joint its upper end is thickened and the lower edge produced outwards and upwards so that they jointly provide a concave articular surface directed upwards for articulation with the interhyal. This is also mostly cartilaginous.

THE INTERHYAL. (Plate 3, I, Hy.). It is through this bone that the hyoid arch is articulated to the skull. It is an irregular rod-like bone articulating by its base to the epihyal at a right angle, and by its apex to the short strut on the inner side of the hyomandibular.

(vi) THE BRANCHIO-STEGAL RAYS. (Plate 3, Br. R. I to V). There are 5 branchio-stegal rays attached to the hyoid arch on either side The first four of them are attached to the ceratohyal and the 5th to the epihyal. The 1st, 3rd and the 4th are rod-like and very long while the 2nd and the 5th are much expanded distally. The 5th one looks more like a thin laminate bone and resembles the sub-operculum. It further resembles a side of a leaf on account of transverse lines looking like its veins.

(vii) THE OPERCULAR BONES : (Fig. 1 & Plate 3). Compared with the [illegible] bones of other fishes the sub-opercular is well de-

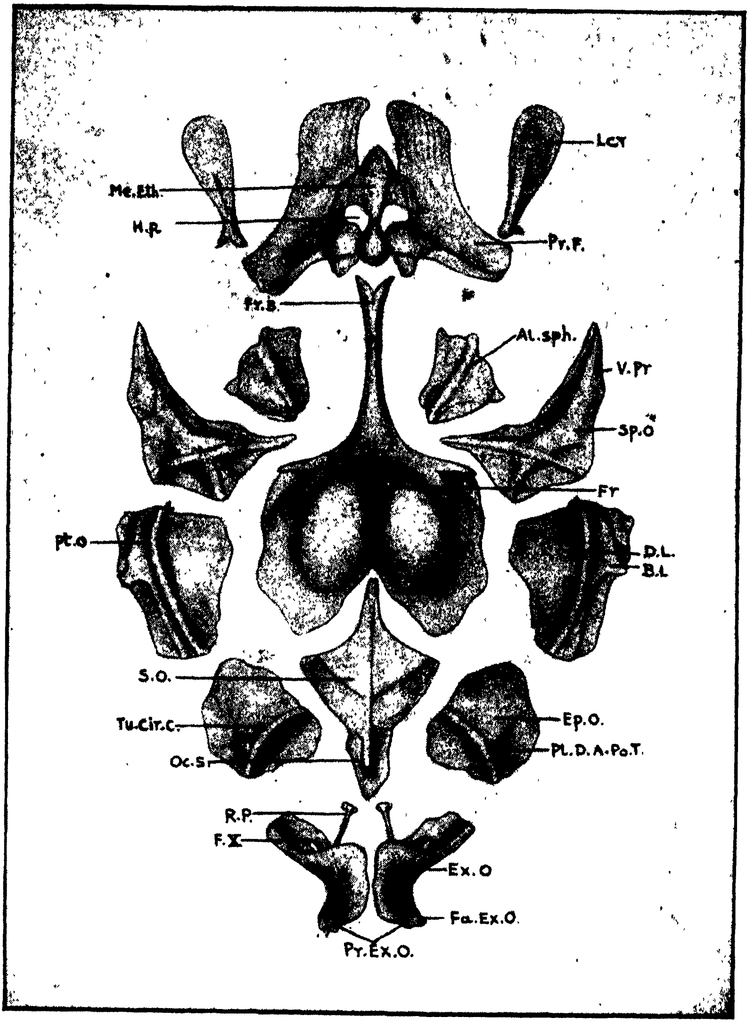


Plate I. Fig. 2. Dorsal view of the disarticulated skull. x16 (with the visceral arches removed).

B. L. = Bony ledge ; H. P. = Foramen for the handle of the palatine ; Lcr. = Lachrymal ; Pr. Ex. O. = Process of the ex-occipital ; R. P. = Rod-like process.

Remaining letters same as in fig. 1.

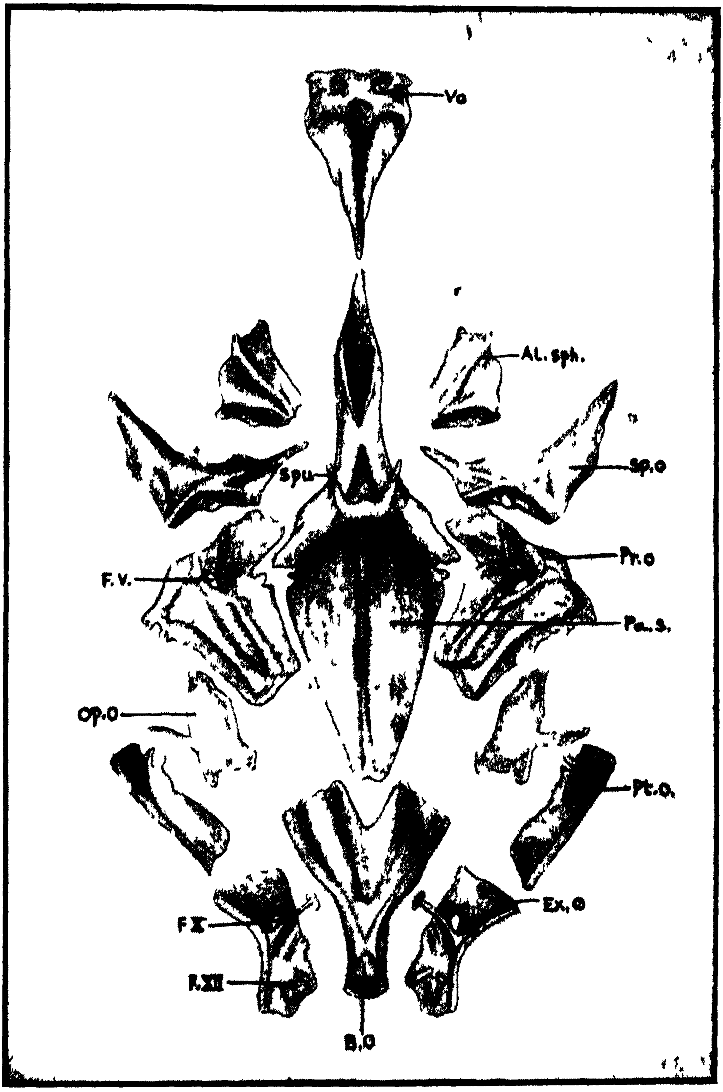


PLATE II FIG 3 Dorsal or cerebral view of the ventral wall of the
disarticulated skull x16
(with visceral arches removed)
Letters same as in fig 2

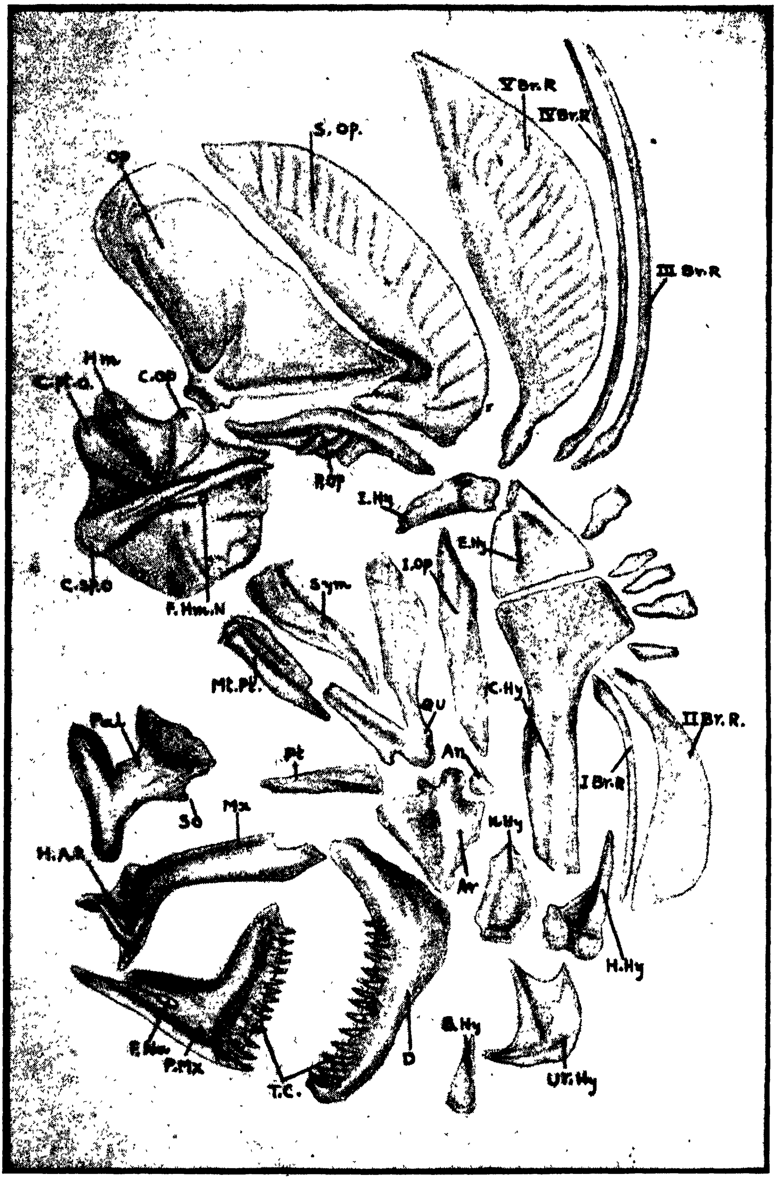


PLATE III. FIG. 4. Lateral view of the disarticulated skull. x16.

B. Hy. = Basi-hyal ; Br. R. I to V. = Branchio-stegal rays 1 to 5 ; C. Op. = Posterior condyle for the opercular ; C. Pt. O. = Middle condyle for the pterotic ; C. S.P. O. = Anterior condyle for the sphenotic.

F. Hm. N. = Foramen for the hyomandibular nerve ; F. Na. = Foramen for the nasal artery ; H. A. P. = Foramen for the anterior process of the palatine ; H. Hy. = Hypohyal ;

I. Hy. = Interhyal; So. = Socket; Sym. = Symplectic; T. C. = Canine teeth; Ur. Hy. = Urohyal.

Remaining letters same as in Fig. 3.

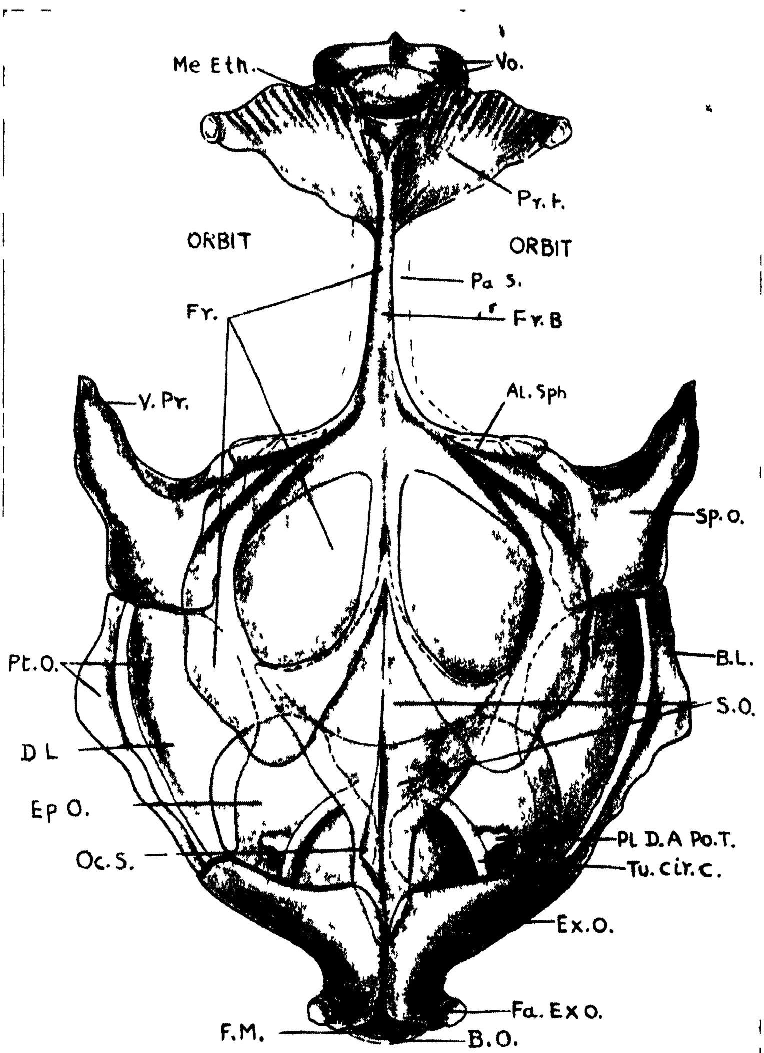


PLATE IV, FIG. 5 Dorsal View of the Skull. x28
(with the visceral arches removed).

Al. Sph. = Alisphenoid, B. L. = Basal ledge; B. O = Basi-occipital;
D L.—Dorsal lamina, Ep. O. = Epiotic; Ex. O. = Ex. O. = Ex-occipital,
Fa. Ex. O. = Facet on the ex-occipital bone; F. M. = Foremen magnum;
Fr. = Frontal, Fr. B. = Frontal bar; Oc. S. = Occipital spine,
Pa. S. = Parasphenoid, Pl. D. A. Po. T. = Platform for the dorsal arm of the post-temporal bone, Pt O. = Pterotic; Pr. F. = Pre-frontal;
S. O. = Supra-occipital, Sp. O = Sphenotic; Tu. Cir. = Tunnel for the posterior semi-circular canal, V. Vr. = Ventral process; Vo. = Vomer.

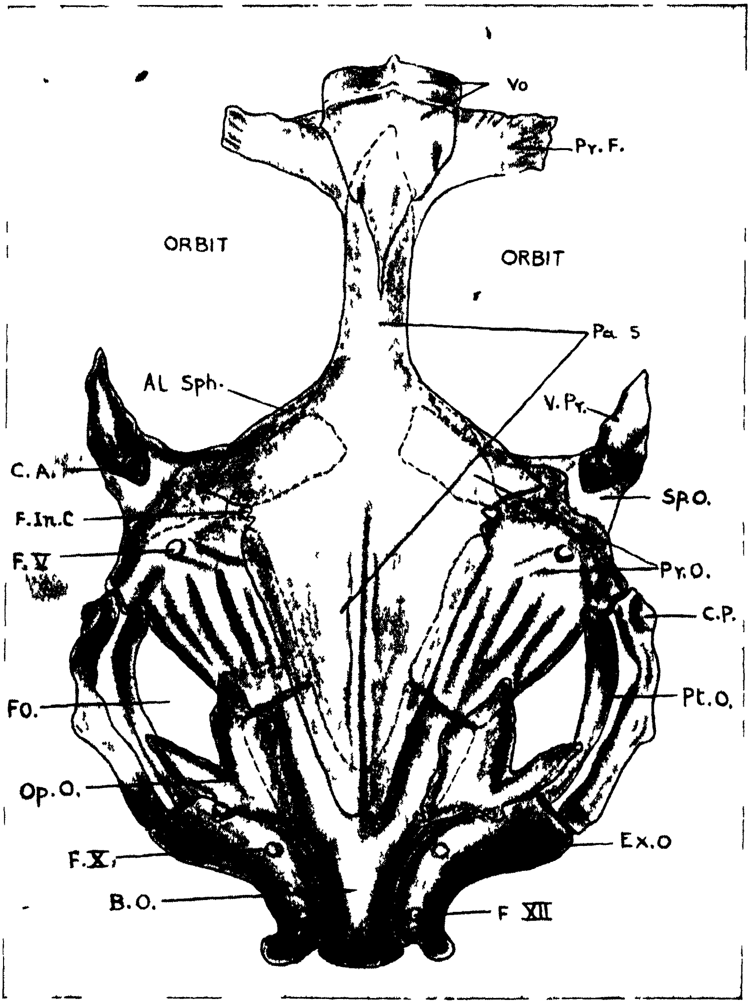


PLATE V. FIG. 6 Ventral view of the skull x 30
(with the visceral arches removed).

C. A. = Socket for the anterior condyle of the hyomandibular;
C. P. = Socket for the middle condyle of the hyomandibular,
F. V. = Foramen for the 5th cranial nerve; F. X. = Foramen for the 10th cranial nerve; F. XII. = Foramen for the 12th cranial nerve;
F. In. C. = Foramen for the internal carotid artery; Fo. = Fontanelle;
Op. P. = Ophisthotic; Pa. S. = Parasphenoid; Pr. O. = Pro-otic;

Remaining letters same as in Fig 1

veloped while the pre-opercular is much reduced. All of them are well ossified.

THE PRE-OPERCULUM. (Fig. 1 & Plate 3, P.Op.). It is in the form of a curved bony rod with a thin flap produced anteriorly in the middle. It firmly joins the hyomandibular and the quadrate, as its dorsal part is attached posteriorly to the vertical ridge of the hyomandibular, and its ventral part lies outside the horizontal arm of the quadrate. It thus forms the ventral and the posterior border of the sub-opercular cavity filled by muscles in living condition.

THE OPERCULUM. (Fig. 1 & Plate 3, Op.). It is a laminar bone thinning out from its articular cup to the margin. Its dorsal side is further produced into a thin membrane. Its articular socket fits well round the posterior condyle of the hyomandibular. Its anterior, vertical margin is thickened into a rod-like ridge. The bone is mostly surrounded by other opercular bones and is cartilaginous only at its articular surface.

THE SUB-OPERCULUM. (Fig. 1 & Plate 3, S. Op.). It is a very thin leaf-like bone situated below the ventral edge of the opercular bone. Anteriorly it bends upwards round the antero-ventral corner of the same. Along its dorsal edge it is thick and gradually becomes thin towards its ventral margin. The ventral half of the bone is traversed by some radiating lines resembling the veins of a leaf.

THE INTER-OPERCULUM. (Fig. I and Plate 3, I. Op.). It is a long, narrow, flattened bone extending between the sub-operculum and the angular. Its posterior end is attached to the pre-operculum and the sub-operculum while its anterior end nearly touches the angular. It is situated below the quadrate and outside the cerato-and epi-hyals.

THE BRANCHIAL ARCHES. The branchial arches will be described in the 2nd part.

BIBLIOGRAPHY.

A complete bibliography will be cited in the 2nd part.

A SHORT NOTE ON THE CILIATED APPARATUS IN THE ECHIURUS LARVA

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This ciliated apparatus was first described by Hatscheck. It was later redescribed by Salensky. Baltzar has described it again in his memoir on Echiurus under the caption of " Flimmerung Apparatus." Conn and Torrey have described a similar organ in a larva of Thalassema.

In order to understand the development of Thalassema by a comparative study, I had obtained, while at Naples, a few larvae of Echiurus some of which were sectioned in different planes and a few more were studied in whole mounts. While examining the series of different sections it became evident to the present writer that the morphological description by Baltzar of this ciliated apparatus through the study of his sections did not seem to be correct. As a matter of fact the older writers appeared to be right in explaining the structure as well as the function of this organ.

According to Baltzar this apparatus consists of a single tube throughout its whole course. It opens into the stomach at one end and into the intestine at the other. Secondly he considers this structure used for carrying a liquid food (Verdauungsleistung) from the stomach to the intestine. While doing so, the tube may carry water which is utilised for respiratory purposes. The same author has made certain experiments by feeding some of these larvae on carmine particles and has found these experiments corroborating his interpretation. These experiments will, however, be referred to later on.

He is supported by Torrey in his above interpretation while working on the larvae of Thalassema.

The older view is on the other hand quite different. This apparatus is, according to that view, made up of two grooves joined together and running side by side throughout the whole course. It is used to carry water inwards from the rectum towards the stomach for respiratory purposes (Atemwasser).

The writer of this note hopes to throw some more light on the complicated structure and the function of this ciliated apparatus. The present description is based upon the study of larvae in the 3rd stage of their development. According to Baltzar this stage is characterized by the presence of two important structures in the form of anal setae and anal vesicles. In this stage the ciliated apparatus seems to reach its highest development.

An ordinary technique has been employed for fixing, sectioning and for staining the material. The picro-formal fluid and hæmatoxylin (Ehrlich) were used as fixing and staining reagents respectively. Sections from 2μ to 4μ thick were cut. Whole mounts were also studied.

The ciliated apparatus consists of two narrow and ciliated tubules joined together. They are not grooves as supposed by Salensky when he describes them as " die Wimperrinne eigentlich aus zwei parallel laufenden Rinne." The median septum is formed by the fusion of the adjoining walls of these tubules which start from the stomach into which they open just near the place where the ventral seta is projecting to the outside through the skin. These tubules are then thrown into 4 or 5 loops on the ventral surface of the intestine during their passage towards the rectum. One of the tubules opens by a short course into the intestine while the other meanders in the shape of groove along the floor of the intestine and opens to the outside through the rectum.

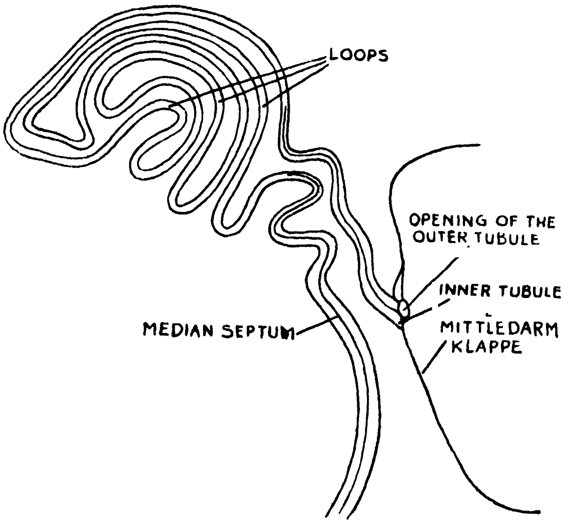

FIG. 1.×80. Showing the loops of the ciliated apparatus.

The loops seem to project antero-ventrally into the body cavity. They are, however, bound together within the outer layer of the ventral wall of the intestine. They can be easily removed and mounted separately without any injury to the intestine. It seems that these tubules may have begun as hollow processes from the stomach and have opened, one into the intestine and the other into the rectum. Between these two ends the tubes have grown longer than the body of the larva and have been therefore accommodated within the cavity by being folded into loops. (Figs. 1 and 2).

The median septum is made up of a double wall from the nature of its formation. It is broader at the base but it tapers

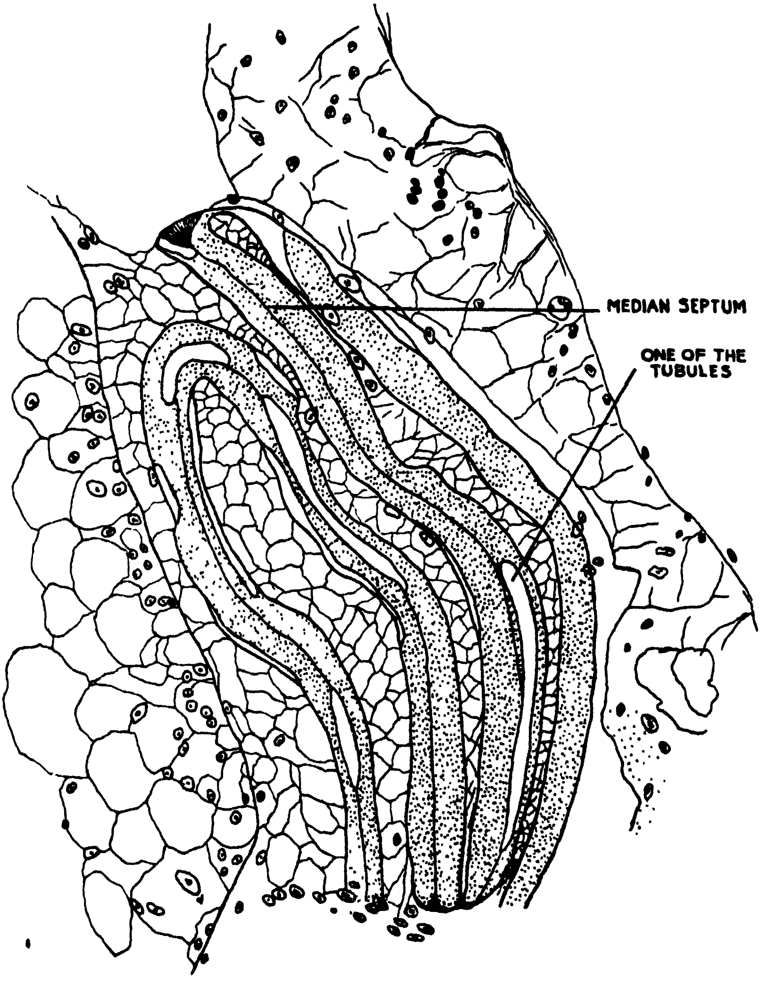

FIG. 2 × 400. A horizontal section of the loops.

distally to a very thin thread-like structure. In a transverse section it appears as if a single tube is divided into two tubules by the growth of the median septum. (Fig. 3).

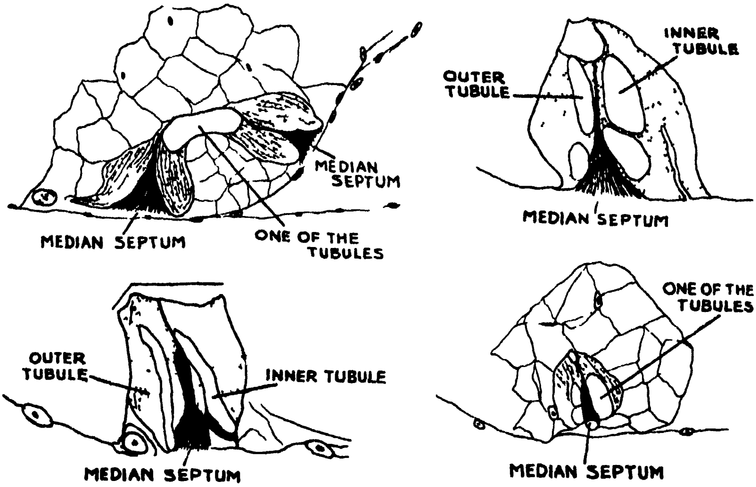

FIG. 3 × 400 Transverse sections of the tubules showing the median septum and two cavities on either side of the septum.

These tubules are arranged in such a way that the shorter of the two opening into the intestine, is found on the inner side of the other which is continued, on the other hand, into a wide groove along the floor of the intestine. This groove, as already mentioned above, runs into the rectum and through the latter to the outside. Each of these tubules can, however, be distinguished from the other by the size and shape of their respective cilia. In the outer tubule the cilia are rather short and stiff, while in the other they are long and limp. In a longitudinal section it will also be seen that the short and stiff cilia seem to bend a little at their free ends towards the anterior end of the animal while the longer and more limp ones appear to curve a little towards the posterior. From this slight bending the direction of a current can be made out. It therefore appears that one current flows in the outer tubule from the posterior to the anterior end of the animal i.e., from the rectum to the stomach; while in the inner tubule on the other hand the current is flowing the other way, i e., from the stomach to the intestine. The outer tubule may henceforward be termed "afferent" while the inner as "efferent" with reference to the stomach. (Fig. 4).

It is mentioned above that both the tubules open into the stomach but the openings are not at the same place nor at the same level. The outer or afferent tubule runs into the stomach at the outer corner of the wall which divides the stomach from the intestine. This dividing wall has been named by Baltzar as the "Mitteldarmklappe." This particular area of the stomach is drawn out into the cavity of the intestine to receive the outer tubule. The lining cells of this area are packed with their well-defined nuclei. The median septum is, however, continued forward beyond the opening of the above tubule and is fused with the inner wall of the drawn out corner of the stomach. This septum is very thin at this place and there is every likelihood of missing it and there is therefore every chance of seeing only one aperture instead of two. (Fig. 6).

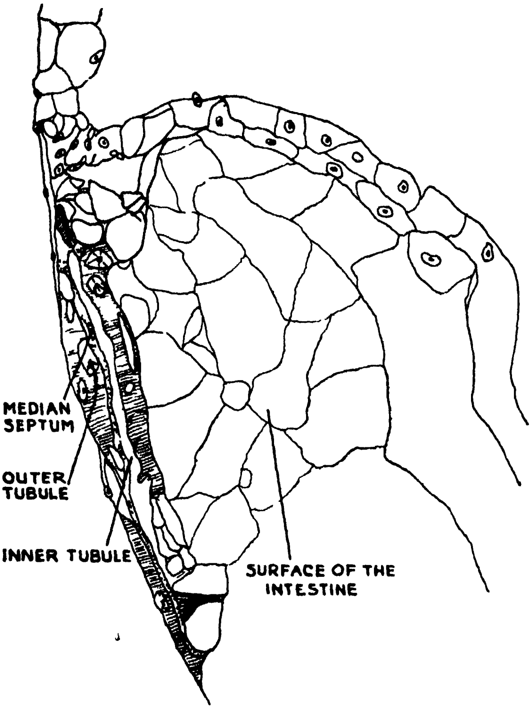

FIG. 4. × 400 A Longitudinal section of the tubules on their way to open into the stomach.

The inner tubule (efferent) which now lies between the median septum on one side and the intestine on the other opens into a slightly bigger cavity than its own lumen, the cavity opening into the stomach. Thus the inner tubule communicates with the stomach through that cavity. From this opening also begins another groove along the base of the Mitteldarmklappe on its posterior side. This groove may be representing the main opening of the stomach into the intestine.

After passing through the loops first towards the anterior and later towards the posterior end of the animal, the two tubules begin to diverge from each other. Just before they do so, the joint tubular area seems to be getting larger. It may be due to the fact that the lumen of each tubule becomes enlarged, especially that of the outer tubule. Within this area the median septum also grows thicker, the epithelial cells becoming bigger and vacuolated. The cilia can be well seen in this area, and their size and shape well marked. (Fig. 7).

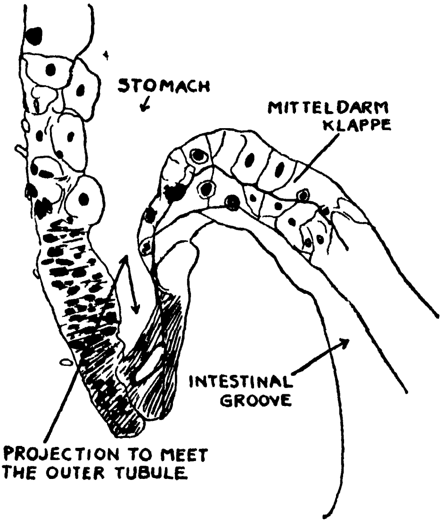

FIG. 5. × 400. A transverse section showing the projection of the corner of the stomach to receive the outer tubule.

The extreme posterior part of this septum which projects as a thin flap over the opening of the inner tubule seems to act as a valve to prevent water coming from the rectum from passing into the inner tubule but which will allow the same to flow into the outer tubule.

It will be seen from the figure that the inner tubule opens immediately afterwards into the intestine while the outer tubule continues its course onwards the rectum. It now loses its tubular character and forms a groove deep and wide along the floor of the intestine. This groove is lined on both of its sides with tall columnar cells provided with cilia. In the centre of the groove there is a well marked group of cells with longer cilia. This groove is then continued along the floor of the intestine towards the rectum. The dorsal wall of the intestine has no such ciliated groove.

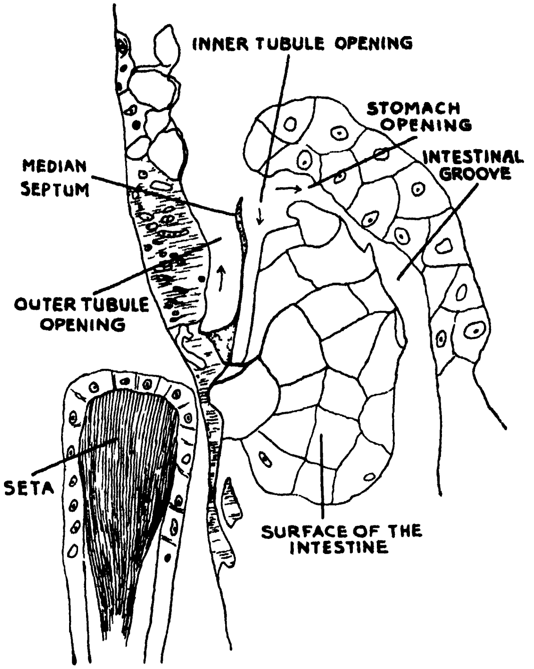

FIG. 6. × 400. A transverse section showing the outer and the inner tubules opening into the stomach.

After passing through the rectum it opens into the cloaca. The anal vesicles which are being developed in this stage also open into this region. The cells lining the groove in the rectum are regularly columnar and ciliated. (Fig. 10).

From the above morphological description and the perusal of some of the figures, it will be seen that the ciliated apparatus of the Echiurus larva consists of two distinct tubules running side by side. The two contiguous walls form the median septum between the cavities of these tubules. It will also be seen that this apparatus is made up of three parts : anterior, posterior and middle. Four or five loops are formed in the middle part, while in the anterior part these tubules open into the stomach in the way already described above. In the posterior part the tubules diverge from each other, the inner of them opening into the intestine and the outer continuing its course towards the rectum along the floor of the intestine. This tubule is modified into an open groove in the latter part of its course.

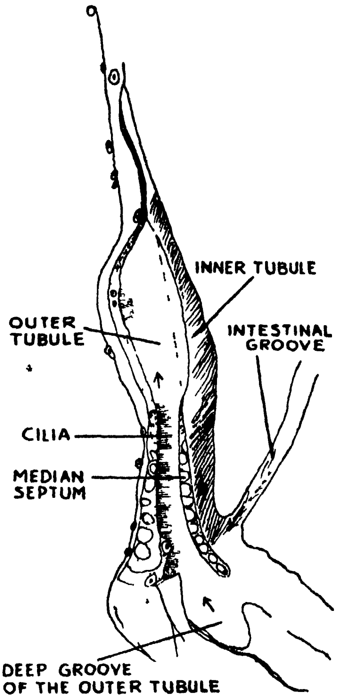

FIG. 7. × 900. A Longitudinal section showing the swollen portion of the tubules, the thickening of the septum and the valve.

The function of this apparatus will be easily understood from the above description. The cavity of the cloaca into which the outer tubule opens is rhythmically enlarged by the contractions of the sphincters. When enlarged, the cloaca can suck in water from outside but the same will be driven into the groove when the cloacal cavity is assuming the normal size by the relaxation of the sphincter muscles. The water once in the groove is propelled forward anteriorly by the movements of the cilia. It now flows from the groove into the outer tubule and ultimately runs into the stomach after passing through the loops.

In the meanwhile the water accumulated in the stomach finds its way into the intestine through the inner tubule of this apparatus and also through the main opening of the stomach into the intestine through the Mitteldarmklappe. This opening seems to be rhythmical in its operation.

Before the experiments of Baltzar are described it is necessary to remember that there are three apertures by means of which the stomach communicates with the other part of the alimentary canal:

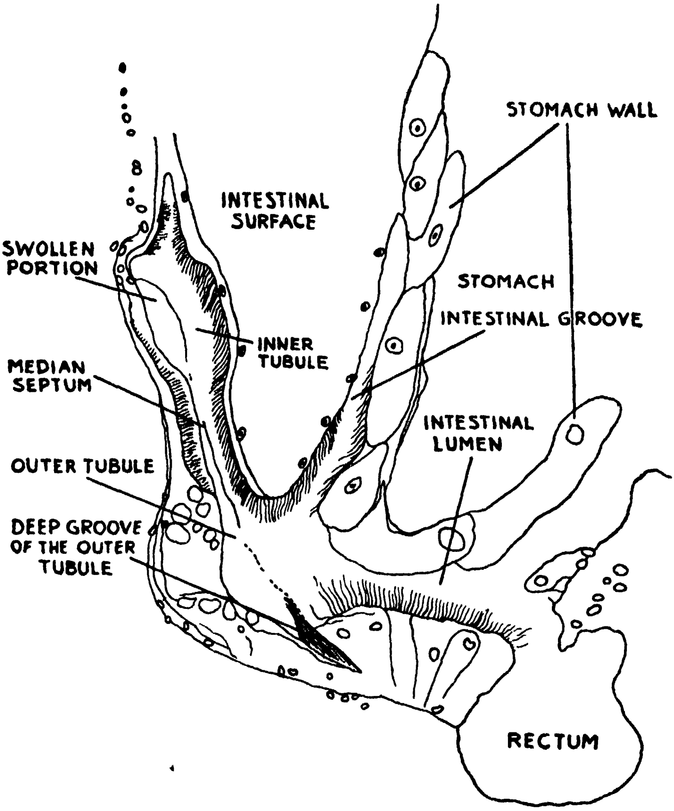

FIG. 8. × 400. A longitudinal section showing the courses of the tubules and other openings into the intestine.

by one of the apertures the stomach communicates with the cloaca through the outer tubule; by the second aperture it opens into the intestine through the inner tubule and lastly by the third aperture which is the main opening of the stomach, the latter opens into the intestine at irregular intervals of time.

Baltzar has made certain feeding experiments on a few larvae of Echiurus in order to determine the function of this apparatus. He fed a few living larvae on carmine particles and after twelve hours or more he found the ciliated apparatus to be red. ("Diese rote Flussigkeit mit kleinen Karminteilchen kursiert durch den Flimmerapparat und zwar ohne Ausnahme in der Richtung von Anus zum Vorderende.") He himself suggests the possibility of few carmine particles entering the apparatus through the anus. On the strength of these experiments Baltzar and others like Torrey and Con maintain that this apparatus is used for transporting food from the stomach to the intestine. To mention the same in the words of Baltzar "Plausibler erscheint es mir, dass die Tatigkeit des Flimmerapparates die Verdauungsleistung des Darmes erhort wird, denn es macht ja der Inhalt des Darmes einen Kreislauf durch ; er gelangt einerseits durch die Offnung der Mitteldarmklappe aus der vorderen in die hintere Darkammer, wodurch auch die festen Bestandteile von Vordern in die hintere kammer transportert werden. Andererseits gelangt die Darmflussigkeit mit ihr auch kleine feste Partikeln des

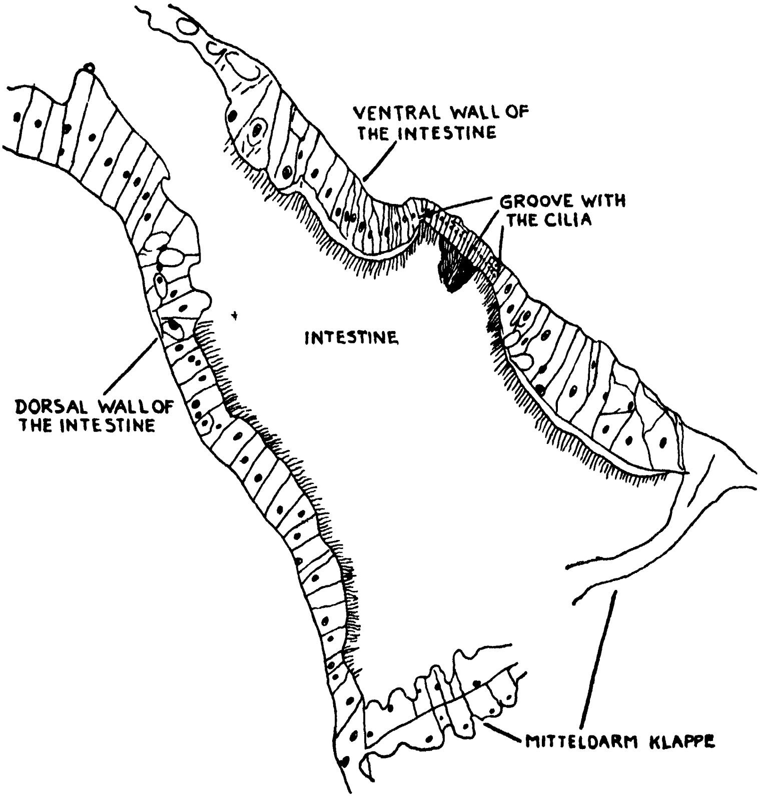

FIG. 9. × 400. A transverse section showing the groove on the floor of the ventral wall of the intestine.

Darminhalts durch die Wimperspirale in die "Osophagealkammer zuruck und der Kreis lauf beginnt von neuem." At the same time this author had been under the impression that there was only one tubule for communication. He had not observed the second, i.e., the outer tubule though Salensky before him as already mentioned above, had referred to the double nature of this tubule. The latter author had, however, not investigated it further.

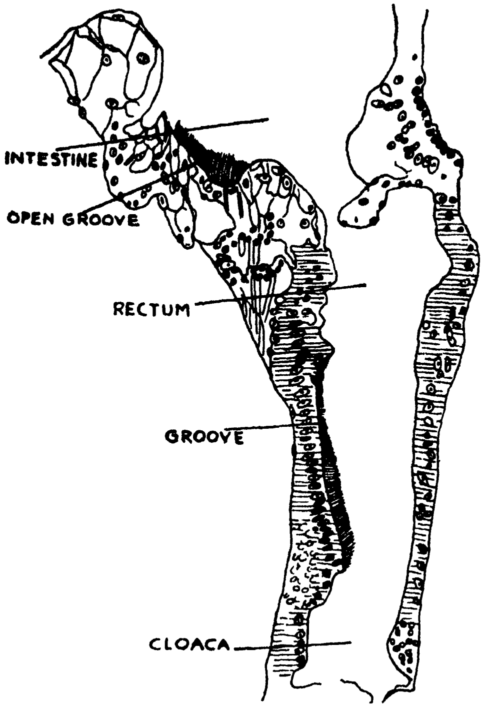

FIG. 10 ×400. A longitudinal section showing the groove in the rectum.

The above experiments by Baltzar may prove one fact that the inner tubule carries liquid food or water from the stomach to the intestine. But they do not go against the existence of the outer tubule, which the present writer has tried to prove in this paper.

This ciliated apparatus may be an "Analage" of a certain structure found in the adult. In the latter there is a groove running along the floor, i.e., on the ventral side of the posterior part of the alimentary canal. This groove is sometimes open and at other times it forms a closed tube. Through this open groove or the closed tube a current of water is constantly flowing from one end (anterior) to the other. During the metamorphosis of a larva this ciliated apparatus may be completely modified : the loops may have become unwound and applied to the ventral wall of the growing and extending alimentary canal. One of the tubules may have been lost in the metamorphosis and only one tubule has been left in the adult. Through this tubule now runs the current of fresh water to be used for respiration in the adult. So in the larva a similar but highly complicated structure like the ciliated apparatus may also have been useful for the same purpose.

I take the opportunity of thanking the Director of the Marine Biological Station of Naples for giving me all the facilities for work and also for obtaining the material for me.

Literature. F. Baltzar. Fauna and Flora of the Gulf of Naples. No. 34.

STUDIES ON THE VASCULAR CRYPTOGAMS OF THE BOMBAY PRESIDENCY.

PART II. DISTRIBUTION OF THE OPHIOGLOSSACEÆ WITH NOTES ON THE ECOLOGY OF THE SPECIES.

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(*with 30 figures*)

CONTENTS.

Page.
I. INTRODUCTORY 104
II. DESCRIPTIVE :
(A) Botrychium 105
(B) Heliminthostachys 107
(C) Ophioglossum 108
III. SUMMARY AND GENERAL REMARKS 113
IV. ACKNOWLEDGMENTS 115
V. BIBLIOGRAPHY 116

I. INTRODUCTORY

In the first part of the present studies, the geographical distribution and ecology of the Psilotaceæ, Equisetaceæ and the homosporous Lycopodiaceæ were considered; the corresponding facts for the Ophioglossaceæ will now be dealt with here. The treatment of the subject-matter will be more in detail than in the previous paper, as I have investigated this family fully with the help of the research grant I received at the hands of the authorities of the University of Bombay. I personally visited and studied a number of places mentioned in the paper and took notes on the ecology of the species in field. I had the benefit of consulting the herbaria of the Royal Botanic Gardens, Sibpur, Calcutta; the College of Agriculture, Poona; the Bombay Natural History Society, Bombay; Gujarat College, Ahmedabad and some others. I also consulted the published literature on the family, and a part of the information incorporated in the paper is derived from it. The present paper puts together the results of my study of this family for the last six years, and aims at presenting the information I have gathered through correspondence, literature, etc., in a systematic manner. It does not pretend to be exhaustive as I believe, there is still room for further investigation of this interesting family of primitive ferns.[1]

II. DESCRIPTIVE

The Ophioglossaceæ and Marattiaceæ constitute a group of ferns called "Eusporangiatæ" by Goebel. The group is an ancient one and has a wide geographical distribution. Fossil record of the Marattiaceæ is admirably clear, just the reverse being true of the Ophioglossaceæ. The living Marattiaceæ are mainly tropical or sub-tropical; the Ophioglossaceæ extend beyond those regions and inhabit the temperate regions also. So far as the Bombay Presidency is concerned, there is only one Marattiaceous fern, viz. *Angiopteris evecta* Hoff. and its consideration may be deferred to some later paper. The Ophioglossaceæ on the other hand are fairly well represented by various forms of their three well known genera, *Botrychium*, *Helminthostachys* and *Ophioglossum*. Of these three, I have not been able to find the plants of the first mentioned two genera, in our Presidency proper, although I have collected a fair amount of them in the adjoining Mysore State, in the Baba Budhan Hills (which form a part of the same range of the Western Ghats which pass through our Presidency). Gray,[2] however, does give them in the Botany of the Bombay Presidency and it is quite likely that we may get them in our Presidency proper in some near future, if carefully searched for.

A. *Botrychium*.

The genus consists of about thirty[3] species out of which the following five occur in India[4] :—

1. *B. lunaria* L.
2. *B. daucifolium* Wall.
3. *B. virginianum* Sw.
4. *B. lanuginosum* Wall.
5. B. ternatum Sw.

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[1] No historical review of literature on the family is given here as I have given it in my another paper on the family, now in course of publication elsewhere. See also Campbell (1911), Bower (1926) and Maheshwari and Singh (1934).

[2] *Bombay Gazetteer*, Vol. XXV.

[3] Prof. Underwood gives thirty species but Bitter (1900) gives only sixteen. Christensen (1906) gives an account of thirty-four species.

[4] Beddome (1883) and Clarke (1880) do not mention the last species. It is included here on the authority of Hope (1903). There are some specimens of this species in the herbarium of the Gujarat College, Ahmedabad. They were collected at Mussoorie in the Himalayas.

Of these five species *B. lanuginosum* is the only species known to occur in the Bombay Presidency.

Botrychium lanuginosum[1] Wall.

(Plate II, Figures 5 and 6.)

Diagnosis : Beddome (1883), p. 471 ; Clarke (1880), p. 588.

OCCURRENCE AND HABIT.

The species is common in the Himalayas, the Nilgiris, parts of the Sahyadris and Ceylon. It grows on the damp humus of forests which have plenty of undergrowth. It is often found in the midst of decaying leaves and stumps of *Bamboos*, and in the *Tectona grandis* plantations. It forms beautiful patches on mossy turfs by the side of small water-courses and knolls at Naini Tal, Ootakamund, Kodaikanal and other hill stations standing on lofty heights. The species appears in the monsoons only. The specimens on which the present account is based were collected on a grassy mound in the Baba Budhan Hills in the Mysore State, in the month of October. At Ootakamund and other places the specimens can be had till the end of November.

As stated above, I have not met the plant in our Presidency proper. But curiously enough, I have seen a specimen of this species in the Calcutta Herbarium, collected at Mount Abu by late Dr. King—the then Director of the Botanic Gardens, Sibpur. This is perhaps the only authentic specimen of *Botrychium* from our Presidency. Unfortunately, as Mr. Narayanaswami informs me, no other information about the plant is available from the sheet or from the record of sheets in the Herbarium. Further search of the plant is a desideratum.

Fig. 5, pl. II shows a plant collected in the Baba Budhan Hills and Fig. 6 on the same plate shows a plant from the Himalayas. The Himalayan specimens[2] are larger than the specimens collected in the Baba Budhan Hills, and are much variable in size.

Distribution : shown in Fig. 1, pl. I.

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[1] Blatter and d'Almeida consider this as a variety of *B. virginianum*. But Milde in his monograph of the genus considers this to be a distinct species. This is also the view of Prantl and Underwood. Both of them regard it not merely as a variety of *B. virginianum* but as a separate species. See Clarke (1880), p. 588 ; and Underwood (1896), p. 464.

[2] I am very thankful to Prof. H. G. Champion, M.A., F.N.I.,—through whose courtesy I obtained the Himalayan specimens of *Botrychium* he had collected at Naini Tal and other places in the Himalayas.

'At the higher elevations in the Western Ghats.'[1]
'Bombay Presidency-Ghats.'[2]
'Mount Abu.'[3]
'Baba Budhan Hills[4] (Mysore State).'
'Agumbe[5] (Mysore State).'

B. *Helminthostachys.*

The genus consists of a single species, restricted more or less to the Indo-Malay region, Ceylon, and Australia. It is known from different parts of India, e.g., plains of Bengal up to Chachar,[6] 24-Pergunnahs,[7] suburbs of Calcutta,[8] Outshahi[9] (Dist. Dacca), Trivandrum,[10] Travancore,[11] Baba Budhan Hills, Southern Konkan, etc. I have not been able to find the plant in our Presidency. The observations recorded below are based on my experience of collecting the plant in other parts of India. But since the genus is monotypic, they should be of use to those that would undertake to search the plant in our Presidency.

Helminthostachys zeylanica Hook.

Diagnosis : Hooker (1874), p. 457 ; Beddome (1883), p. 467 ; Blatter and d'Almeida (1922), p. 203.

OCCURRENCE AND HABIT.

The plant is a semi-marsh plant. It grows in damp clayey swamps, monsoon pools, or below trees like *Mangifera indica, Tectona grandis,* intermixed with shrubs. At Calcutta, it was found in the midst of what may be called *Glycosmis pentaphylla* association. In the vicinity were many other ferns also ; conspicuous amongst them were *Lygodium flexuosus* and *Adiantum caudatum*—the common marsh ferns. The species is often found on the plains but it is

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1. Beddome (1883), p. 472.
2. Gray, *Bombay Gazetteer,* Vol. XXV.
3. Herb. Roy. Bot. Gard. Calcutta. This specimen was collected at Mount Abu by Dr. King in 1868 (Mr. V. Narayanaswami's letter to the author dated 16th August, 1937).
4. Dr. M. A. Sampathkumaran, 1932 ; Mahabale, 1935, 1936.
5. Prof. L. Narayana Rao, 1935.
6. Beddome (1883), p. 469.
7. Prain, D. (1908).—The Vegetation of the Districts of Hughli-Howrah and the 24-Pergunnahs. Records of *Bot. Survey of India,* Vol III, p. 326.
8. Muzumdar (1930), p. 289.
9. Prof. Mukundalal Chakrawarti (1936), Calcutta.
10. Dr. Sampathkumaran (1934).
11. Dr. E. K. Janaki Ammal's letter to the author, 26th August, 1937.

not restricted to plains only. It can be had in the hills up to about 3000 feet elevation. Clarke (1880) in his 'Review' says, "I have never met the plant in the hills even 250 feet above the sea. I believe the locality Himalayas given in Hooker and Baker's Synopsis Filicum is erroneous." But the fact that the plant has been gathered in the Baba Budhan Hills more than 3,000 feet above the sea level, is sufficient to indicate the mistake in Clarke's statement quoted above. I have seen some specimens collected in the Garo Hills (Assam Himalayas) in the herbarium of the Gujarat College, Ahmedabad.

Distribution : shown in Fig. 1, pl. I.

'Baba Budhan Hill[1] (Mysore State).'

'In swampy places in Southern Konkan.'[2]

C. *Ophioglossum.*

This cosmopolitan genus of the family has about forty-three[3] species spread all over the world. There is no definite agreement amongst the workers in India as to the number of our native species. This is largely due to labile nature of the characters used to separate the species. The whole genus badly needs a careful revision. For the purposes of the present studies, I have mainly followed Hooker and Baker's 'Synopsis Filicum', although references to later authors like Beddome, Clarke, Blatter and d'Almeida were indispensable.[4]

The following species were collected in the Presidency :—

1. *O. reticulatum* L.
2. *O. vulgatum* L.
3. *O. pedunculosum* Desv.
4. *O. aitchisoni* d'Almeida.
5. *O. fibrosum* Schum.
6. *O. nudicaule* L.
7. *O. gramineum* Willd.

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[1] Dr. Sampathkumaran, (1936).

[2] Gray, *Bombay Gazetteer, Vol. XXV*. Blatter (1908) quotes this locality. But the term 'Southern Konkan' is too extensive. I have made a very careful survey of the famous Agrapara locality near Calcutta in the company of a botanist friend of mine, Mr. R. N. Dutta, M.Sc. and I am inclined to think that Calay, suburbs of Goa, Vetora and similar places in Sawantwadi State are the proper places to search for *Helminthostachys* in Southern Konkan.

[3] Hooker (1874).

[4] I am aware of the fact that a modern treatment of the genus would require some important changes in Hooker's classification. This I hope to do in my another paper dealing with the species problem. I have followed Hooker mainly because, my findings agree mostly with him.

It will be noticed from the above list, that we have all the Indian species of the genus, except epiphytic *O. pendulum*, found in Assam and Ceylon.

1. *O. reticulatum* L.

(Plate III, Figures 15 and 16 and Plate V, Figure 22.)

OCCURRENCE AND HABIT.

The species is mostly found under the shade of trees and bushes on the hills. It is found under similar conditions on plains also, e.g., at Calcutta. At Purandhar (Dist. Poona) and on the Nandi Hills near Bangalore, the species is found in abundance under the thickets of *Lantana camara, Cæsalpinia pulcherrima* or near the trunks of *Caesarina equisetifolia*. The growth of the plants is so rich here, that the fronds sometimes reach a height of 14 inches or more. The species, therefore, is to be regarded as one of the largest living *Ophioglassums*. The leaves in all adult specimens, small, or large, were cordate and hafted (See Fig. 22, pl. V).

Distribution : shown in Fig. 1, pl. I.

Purandhar[1] (Dist. Poona); 'under the thickets of *Lantana camara.*'

North Kanara ;[2] Birchi.[3]

'In grassy places on the Ghat.'[2]

Baba Buddhan Hills.[5]

Bannergadh,[4] Nandi Hills[5] and other places near Bangalore (Mysore State).

2. *O. vulgatum L.*

(Plate III, Figures 13 and 14.)

Diagnosis : Hooker (1874), p. 445 ; Beddome (1883), p. 464.

OCCURRENCE AND HABIT.

The species is found on the margins of lakes, pools, the banks of rivers, etc., in grasses. The plants begin to put forth fronds in the month of June after the rains and last till the end of April in suitable places. Spikes are formed once in August and again in January-February ; in the latter case they last till the end of March. In garden the species thrives well all the year round. So far, I have not met the species in the hills. It mostly resides on the plains.

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[1] Mahabale, 1932.

[2] Gray, *Bombay Gazetteer*, Vol. XXV.

[3] Herb, Agr. College, Poona, (Talbot's collection).

[4] Mr. Gopal Iyengar, Bangalore.

[5] Dr. Sampathkumaran ; Mahabale, 1935.

Distribution : shown in Fig. 1, Pl. I.
Vithhalwadi ;[1] 'on the banks of the Mutha River.'
Ganeshkhind ;[2] 'common on the margins of ponds.'

3. *O. pedunculosum*[3] Desv.

(Plate IV, Figures 26, 27, 28, 29.)

Diagnosis, Hooker (1874), p. 466.

OCCURRENCE AND HABIT.

This little known species from Peninsular India was found to grow on mounds of organic debris collected near Khadak—a well known rocky place near Poona. The species was also found to grow in pasture lands near a village, Katraj. The soil on which it grew was rich in humus content, and was a waste land. *Achyranthus aspera, Celsia coromadeliana, Argemone mexicana, Gynandropis pentaphylla* and other members of a typical waste-land community were present in the vicinity. The species thrives well if the rains are heavy. The plants are distinctly polyphyllous and produce as many as eight leaves in a season.

Distribution : shown in Fig. 1, pl. I.
'Peninsular India.'[4]
Khadak [5] near Poona.
Parwati[6] village (Dist. Poona) ; 'Common on pasture grounds.'
Katraj[6] (Dist. Poona); 'on the outskirts of the village.'

4. *O. aitchisoni d'Almeida.*

(Plate III, Figures 7, 8, 9.)

Diagnosis : d'Almeida (1922), p. 63.

OCCURRENCE AND HABIT.

This is the commonest of all the species in our Presidency. It is widely spread over the plains, not only in this part of the country but in other parts of India also, e.g., the plains of Punjab. It is very hardy and grows in a variety of situations, although one often finds it on gravelly, calcareous soils. It appears immediately after the first showers of rain and lasts till the end of November. The species has a decided tolerance for dry conditions. It is most common in and about Poona, on open, sunny grass-lands.

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[1] Mahabale, 1936.

[2] Mahabale, T. S. and Kanitkar, U. K., 1934.

[3] See Mahabale (1937).—The Gametophyte of *O. pedunculosum* Desv. Proc. Ind. Sci, Con. Hyderabad, 1937, p. 256.

[4] Hooker (1874), p. 466.

[5] Deshpande, G. S., and Bavadekar, V. G., 1933.

[6] Mahabale, 1933.

Distribution : shown in Fig 1, pl. I.

Siroor[1] (Dist. Poona), 'near horse breeding station.'

Otur[2] (Dist. Poona), 'common in grasses on sandy soils.'

Poona,[3] 'in the compound of the Fergusson College. On the slopes of the Fergusson College Hill.' Chaturshingi[4] and Parwati Hills near Poona, 'at the foot of the hills.'

Kolhapur,[5] 'along the railway line.'

Shrigonda (Dist. Ahmednagar), 'near the old temples on the Saraswati River.'

Ahmednagar,[7] 'near the fort.'

Saswad[8] (Dist. Poona), 'generally below the trees of *Ficus benghalensis.*'

5. *O. fibrosum* Schum.

(Plate III, Figures 10, 11, 12.)

Diagnosis : Beddome (1883), p. 465. Blatter and d'Almeida (1922), p. 202.

OCCURRENCE AND HABIT.

The species is usually found in the hills having heavy rains. It grows on the soil collected in the ditches in rocks by the side of small water-courses running down the trap hills. Such a soil being mostly formed of large rock-particles and clay, there is profuse development of fibrous roots, characteristic of the species. Perennial corm of this species strongly recalls to one's mind the appearance of the protocorm[9] in *O. Pringlei* Underwood, a species from Mexico. At Lonawala the plants reach a height of 9-10 inches. Like *O. reticulatum* the species is one of the large species of *Ophioglossum.*

Distribution : shown in Fig. 1, pl. I.

Khandala[10] (Dist. Poona).

Lonawala[11] and Bhangarwadi[12] (Dist. Poona), 'along the water-courses.'

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1. Chakradeo, 1920.
2. G. S. Deshpande, 1933.
3. Mahabale, 1930.
4. U. K. Kanitkar, 1933.
5. G. S. Deshpande, 1937.
6. and 7. Mahabale 1931, 1932.
8. T. S. Mahabale and Y. B. Raje, 1932.
9. Land (1911). A Protocorm of *Ophioglossum*. *Bot. Gaz.*, Vol. LII, pp. 478-479.
10. d'Almeida (1922), p. 64.
11. Mahabale, 1932.
12. Prof. V. V. Apte, 1933.

Murrol[1] Hill near Bombay.
Trombay[1] Hill near Bombay.
Canary[1] Islands near Bombay.
Alibag[2] (Dist. Kolaba), 'on the hills.'
Bandhan sub-station of the agricultural Farm near Alibag.[3]

6. *O. nudicaule* L.

(Plate IV, Figures 17, 18, 19, 20, 21)

Diagnosis: Beddome (1883), p. 464; Blatter and d'Almeida (1922), p. 200.

OCCURRENCE AND HABIT.

The species occurs in stray patches in grasses, on slopes of hills and on lawns. Very often it grows with some other species of *Ophioglossum*; for example, at Khandala and Lonawala it grows with *O. fibrosum*; at Purandhar it grows with *O. reticulatum*. Like *O. fibrosum* the species grows in soils saturated with water. It appears in the monsoons only. It quickly disappears after the rains. It can hardly be collected in the month of October. The species is remarkable for its gregarious habit. Within a short space of one square inch, two or three plants can be seen. It is one of the smallest *Ophioglossums*. Hooker's description of this species does not hold good for the Indian plant. Indian *O. nudicaule* is a much smaller fern, than what Hooker describes (See Figs. 18, 21).

Distribution shown in Fig. 1, pl. I.
Khandala[4] (Dist. Poona).
Lonawala[5] and Karla (Dist. Poona), 'common on the hills.'
Raita[6] near Kalyan.
North Kanara,[7] 'below ghats.'
Karwar,[8] 'in the rains.'
Castle Rock.[9]
Purandhar[10] Hill fort (Dist. Poona), 'common on rocks.'
Bomanhulli[11] (North Kanara ?).

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[1] Mr. C. McCann, 1935.

[2] Prof. D. L. Dixit, 1912.

[3] Prof. R. K. Bhide, Herb. Agr. College, Poona (The specimens are wrongly labelled as *O.vulgatum*).

[4] Blatter and Hallberg, 1919.

[5] Bhide V. V. & Gupte D. R. 1933.

[6] Dr. F. R. Bharucha, 1938.

[7] Herb. Bom. Nat. Hist. Soc. Bombay; Macpherson (1894), p. 375; Blatter (1908), p. 611.

[8] Herb. Bom. Nat. Hist. Soc. Bombay.

[9] Sedgwick and Bell, 1918; Herb. Gujarat College, Ahmedabad.

[10] Mahabale, 1933.

[11] Herb. Agr. College, (Talbot's collection) Poona.

7. *O. gramineum* Willd.

(Plate IV, Figures 30, 31, 32, 33.)

Diagnosis : Hooker (1874), p. 445 ; Dixit and Mahabale (1934), p. 300.

OCCURRENCE AND HABIT

The species is found in the midst of dense patches of grasses. Sterile lamina of the plant resembles the surrounding grasses so much that one often fails to recognise it. This is a sort of mimicry. The species completes its life-history within a very short time. It is [illegible] first to appear and also the first to disappear. The species grows [illegible] open places on gravelly ground and rock. This species differs from *O. lusitanicum* proper (see Figs. 23, 24, 25, pl. IV.).[1]

Distribution : shown in Fig. 1., pl. I.

Purandhar[2] (Dist., Poona), 'on the rocks in the vicinity of the village at the foot of the hill fort.'

Khandala[illegible] (Dist. Poona), 'on rocks and gravelly places *en route* to Lonawala by old Khandala road.'

III. SUMMARY AND GENERAL REMARKS

The foregoing pages give an account of the Ophioglossaceæ of the Bombay Presidency. They include, *inter alia*, notes on the ecology and geographical distribution of *Botrychium lanuginosum*, *Helmithostachys zeylanica* and seven species of *Ophioglossum* found in the Presidency. A critical examination of the species shows that they represent two diverse elements in the Fern-flora of Bombay. *O aitchisoni*, *O. fibrosum*, *O. nudicaule* and *O. gramineum* represent the African element while *O. reticulatum* and *O. pedunculosum* represent the element of Indo-Malayan origin. *O. vulgatum* is a cosmopolitan species. No endemic forms were found in the area studied.

Next, one finds that all the species of *Ophioglossum* found in the Presidency are terrestrial and belong to sub-genus '*Euophioglossum*' of Prantl. Species belonging to other two sub-genera '*Ophioderma*' and '*Cheiroglossa*' are not found at all. The species of sub-

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1. I have compared the specimens of *O. gramineum* with me with the specimens of *O.lusitanicum* (collected at Madras by Prof. T. Ekambaram, and identified at Kew). I find that *O. gramineum* differs in some respects from *O. lusitanicum*. I, therefore, believe that they are two separate forms. Figs. 23, 24, 25, pl. IV are given here for comparison. My best thanks are due to Prof. Ekambaram for the specimens of *O. lusitanicum* he kindly sent to me.
2. Mahabale, 1933.
3. Mahabale, 1934.

genus '*Euophioglossum*' studied here could be roughly placed under two headings: (1) large forms and (2) small forms. The sterile lamina in large forms is broad and expanded. There is a tendency towards monophylly in large-leaved, large forms and towards polyphylly in small-leaved, small forms. The question now arises here as to whether small forms are to be regarded more primitive than large forms or *vice versa.*

There was a considerable reduction in the size of plants in fossil lycopods and Equiseta. One would expect the same thing to have happened in the case of ferns also. On this supposition the small forms of Ophioglossum should be considered as reduced forms. This is quite possible since the species are mycorrhizic.[1] But the evidence offered by another ancient family, which is also mycorrhizic—the Psilotaceæ, would lead us to an altogether different conclusion. Small forms with small leaves need not always be reduced; they might as well be primitive. The Small forms of *Ophioglossum* in that case should be considered to be primitive, a conclusion just the opposite one of what we have already drawn! Which one of the two rival conclusions is correct, it is rather difficult to decide at this stage. I for one want only to suggest here, that there is a third possibility also. The small species of *Ophioglossum* are perhaps a heterogeneous group, formed partly by reduced forms and partly by primitive forms.[2]

Now as regards the duration and habit, all the seven species studied are geophilous and mycorrhizic. Rhizome is a permanent structure in them; it helps the species to perennate and survive in places otherwise difficult to live in. The rhizome is deep-seated in soil in *O. aitchisoni, O. reticulatum, O. gramineum* and *O. vulgatum*; it is only an inch or so below the soil in *O. fibrosum, O. nudicaule,* and *O. pedunculosum.* Species like *O. nudicaule* and *O. fibrosum* grow in loose soils saturated with water but poor in nutrition; *O. aitchisoni* and *O. gramineum* grow in more or less dry open places; the remaining three species thrive on open, sun-lit lawns—undoubtedly the best places for Ophioglossums to grow and lead a symbiotic life.

All the species appear in the monsoons and last till the end of October. Under natural conditions *O. nudicaule* and *O. gramineum* are the first to disappear, *O. aitchisoni* the last. *O. vulgatum* lasts all the year round in favourable places. Under artificial conditions, *O. reticulatum*, *O. vulgatum* and *O. aitchisoni* give a crop after crop every four months. Attempts to break the dormancy of rhizomes in other species were not very successful. All the species except *O. fibrosum* propagate freely by means of root-buds. The phenomenon is markedly clear in *O. nudicaule*, *O. pedunculosum* and *O. vulgatum.*

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[1] See Bower (1908), pp. 477-479; see also his paper on *O. simplex,* Ridley. Ann. Bot. Vol. XVIII, 1904.

[2] It would be extremely interesting to follow the argument further. But that lies beyond the scope of the present paper.

Study of the geographical distribution of the species of *Ophioglossum* shows that they are unevenly distributed in the hills and on the plains of the Presidency (except Kathiawar and Gujarat). *O. reticulatum* is spread on the hill tops of the Sahyadris, from where it sometimes migrates to the plains. *O. fibrosum* and *O. gramineum* are restricted to the hills only. *O. vulgatum* occurs on the plains.. *O. nudicaule and O. pedunculosum* occur on the plains as well as on the slopes of hills. *O. aitchisoni* is found on the plains only. What do these facts suggest? To me they rather indicate that some species must have reached the plains of the Presidency earlier than others, possibly in different geological periods. Consequently some of them have occupied larger areas on the plains while others are still in a state of exodus from their head-quarters, now pretty obscure to decide. It is necessary, of course, to correlate these facts with the distribution of the same species in other parts of India and the globe also to yield some tangible results. But one fact stands out clear here : the species of African origin and the species of Indo-Malayan origin have a differential distribution in the Bombay Presidency.

Data regarding the distribution of *Botrychium* and *Helminthostachys* in the Presidency are too scanty to analyse. No attempt, therefore, has been made to interpret them.

IV. ACKNOWLEDGMENTS

Greater part of the work embodied in this paper was carried out in the laboratory of the Fergusson College, Poona. My best thanks are due to Principal G. S. Mahajani, M. A., Ph.D. (Cantab.) and Prof. D. L Dixit for the use of unrestricted facilities they gave me in the Fergusson College. I am very grateful to the authorities of the University of Bombay for the research grant they gave me to pursue this work. My thanks are also due to the authorities of various herbaria for allowing me to study the sheets in their charge. Dr. M. A. Sampathkumaran, M.A., Ph.D., gave me many facilities to work in the Central College, Bangalore and I thank him sincerely. Mr. V. Narayanaswami, M.A., and Mr. S. R. Godbole, B.Ag., M.Sc., gave information from time to time about the herbarium sheets in Calcutta and Poona respectively, and I thank them both. Mr. R. G.

Kharadi, B.Sc., helped me in taking the photographs illustrating this paper and I thank him also.

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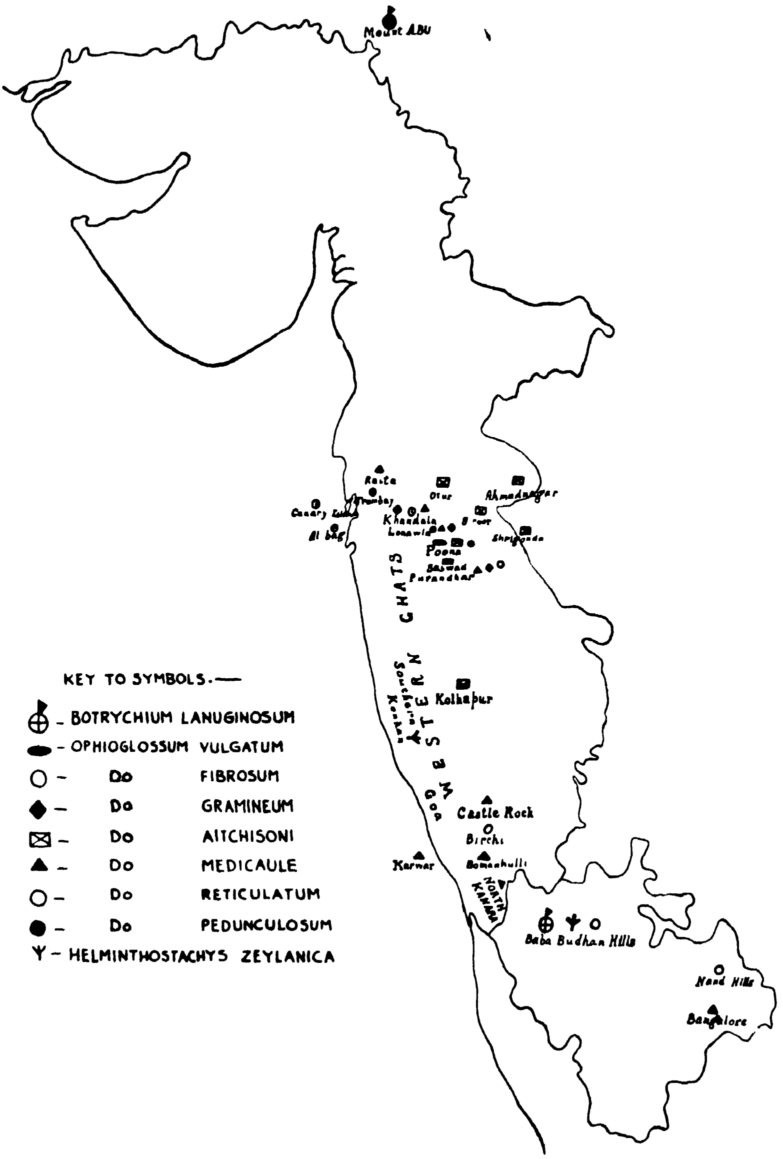

PLATE I. FIG. 1. Map showing the distribution of the species of *Botrychium, Helminthostachys* and *Ophioglossum* in the Bombay Presidency.

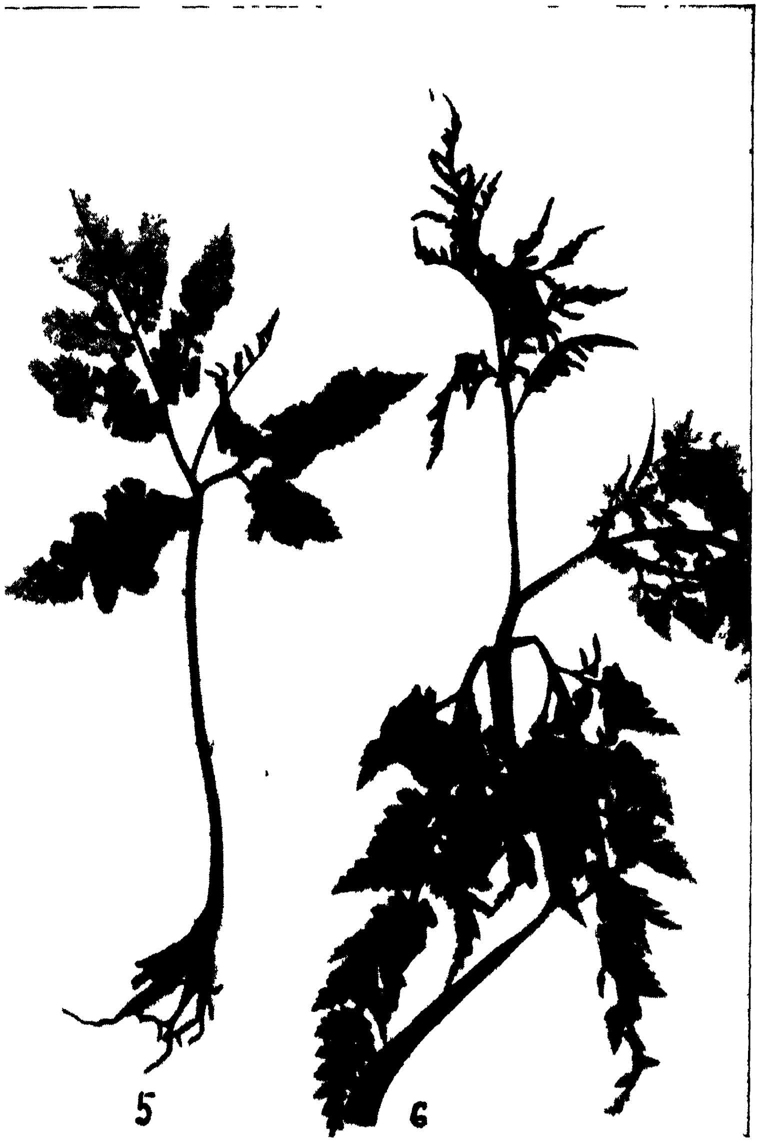

PLATE II. FIGS. 5 and 6. *Botrychium lanuginosum* Wall (½ Natural size). Fig. 5—a plant collected in the Baba Budhan Hills (Mysore State), Fig. 6—a plant collected in the Kumaon Himalayas. Note that the Himalayan plant is larger than the one collected in the Baba Budhan Hills. In both the plants the fertile division arises a little above the sterile lamina.

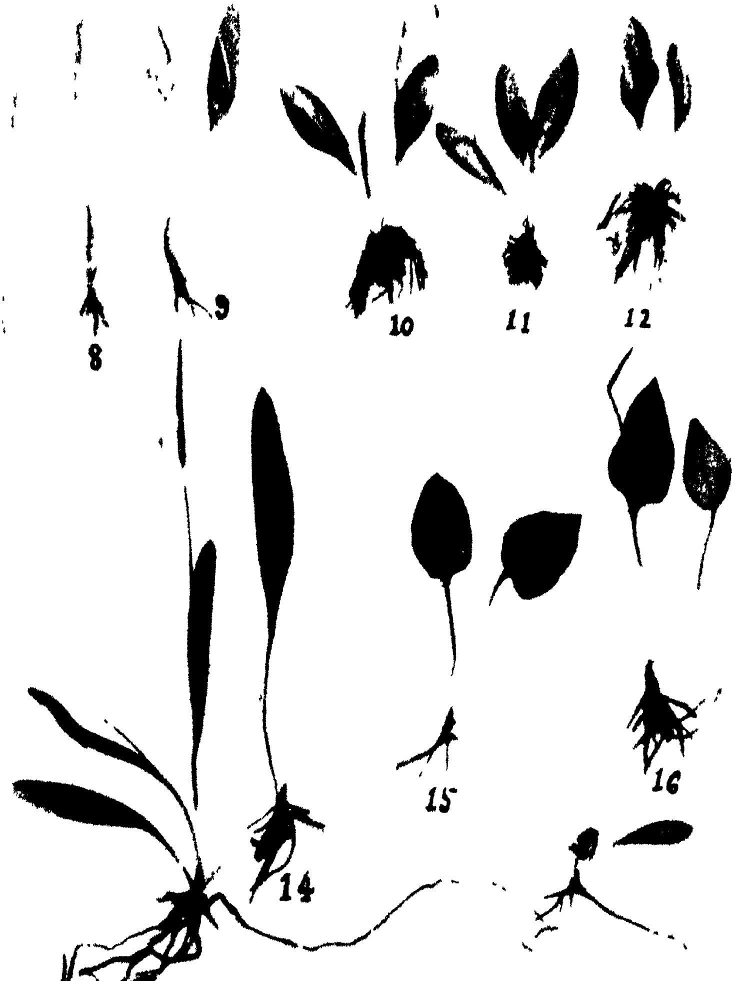

PLATE III. FIGS. 7-16. Species of *Ophioglossum* collected in the Bombay Presidency. ½ Natural size.

FIGS. 7-9. *O. aitchisoni* d' Alm. ; Figs. 10-12. *O. fibrosum* Schum ; Figs. 13-14. *O. vulgatum* L. ; Figs., 15-16 *O. reticulatum* L. Note the root-bud in Fig 13.

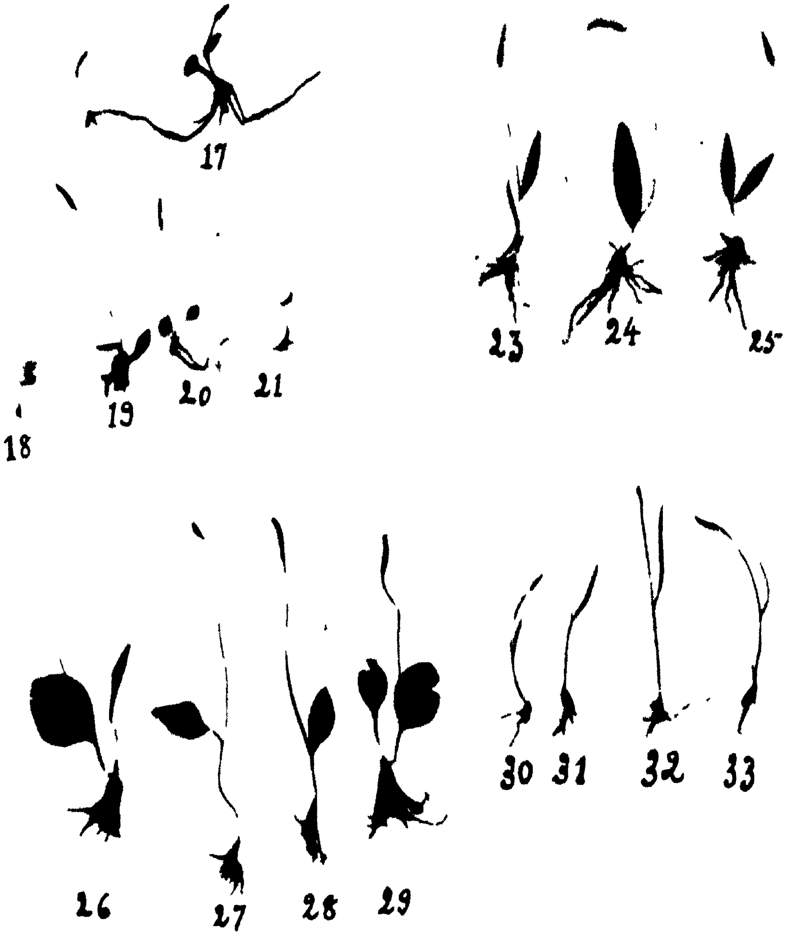

PLATE IV. FIGS 17-21 and 23-33. Species of *Ophioglossum* collected in the Bombay Presidency except Figs. 23, 24, 25, collected in the Madras Presidency. $^2/_3$ Natural size. Figs. 17-21. *O. nudicaule* L.; Figs. 23-25. *O. lusitanicum* L.; Figs. 26-29. *O. pedunculosum* Desv.; Figs. 30-33. *O. gramineum* Willd. Note the root-bud in Fig. 17.

PLATE V FIG 22 *O reticulatum* L growing in a large garden pot below a species of Croton Note the height and cordate lamina of the plants ½ Natural size

(Photograph obtained through courtsey of Dr M A Sampathkumaran, M A, PH D, Bangalore)

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DEVELOPMENT OF THE FEMALE PROTHALLIUM IN AZOLLA PINNATA, R. BROWN

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Introduction. Though much work on the life-history of different species of Azolla has been done by several investigators as Strasburger,[11] Berggren,[1] Campbell[5] and recently by Sud[12] and Rao,[10] it seems that many essential points still remain to be investigated into especially the development of the male and female prothalli. It was under these conditions that the present work was undertaken by the author.

Technique :—*Azolla pinnata* used for investigation was introduced from Baroda and grown in the Botanical gardens, Sind College, Karachi. When the plants produced sporangia they were taken out from the tanks and were kept in the Laboratory in big glass jars. The megasporangia and the microsporangia which were deposited to the bottom by these plants were picked up and put into smaller glass jars or watch glasses as required. Flemming's strong fixative was used for the megasporocarps and microsporocarps. Bouin's fluid also was used with satisfactory results. It was also found that if the infiltration period was lengthened to about seven days, it gave very satisfactory results. Sections were cut from four to eight μ in thickness as required. The stains used were iron-alum-hæmatoxylin and iron-alum-hæmatoxylin with acetic acid. They gave excellent results. Safranin and gentian violet were used both as single and double stains.

Work—The megaspores are borne singly in the megasporangia. When the indusium decays the megasporangia are set free with the upper portion of the induism persisting as a sort of cap. This sporangium freed from the plant immediately sinks to the bottom. Campbell[5] says "The macrospores germinate most promptly in the early autumn, and in California where this species (*Azolla filiculoides*) is abundant, this is probably the natural time for germination." In the species under consideration the megaspores can germinate any time from the middle of December to the middle of April. This species multiplies a good deal by vegetative reproduction and produces sexual organs throughout the above mentioned period.

The first stages of germination of the megaspore take place within the completely closed spore though it is not impossible to say when the germination is about to start. A sure sign of megaspore germination is the complete formation of the float corpuscles. When the float corpuscles are formed and stand out from the megaspore, the megaspore is germinating. In the young stages the female prothallium of Azolla pinnata is not visible externally but its existence can always be made out by the peculiarly characteristic appearance of the megasporangium in the later stages of development.

The development of the prothallium does not begin immediately after the megasporangium sinks to the bottom. It takes a long time. The formation of the float corpuscles takes about twenty days, and after this the formation of the prothallium begins. In all about twenty-five to thirty-five days are required from the time the megasporangium is liberated from the plant to the complete archegonium formation.

At the time of germination the nucleus increases in size and becomes nearly globular. The cytoplasm around this nucleus in the upper portion of the spore does not show in the early stages the large granules characteristic of the lower portion of the spore. The upper portion is cut off from the rest of the spore cavity in a plane which cannot be called exactly transverse. This outer and smaller cell cut off from the spore cavity becomes the mother cell of the prothallium. After a few cells have been formed an apical cell is established, and the further growth of the prothallium is due to this apical cell. Sometimes I find that the prothallium is lobed (M. P. No. 4). Formation of these two side lobes of the prothallium is due most probably to two apical cells at the two sides. These lobes of the prothallium are often not distinct and they do not come to the same height towards the indusiate cap, but at the sides they are higher up than the rest of the prothallial portion.

The cells in the basal part of the prothallium are sometimes elongated in a direction which is parallel to the longitudal direction of the megasporangium.

In a few cases cell formation is seen in the lower part of the spore. This formation is seen when the prothallium is almost ripe. (M. P. No. 2). I believe this is an artifact as it is seen in a very few slides, and further work is needed before anything can be definitely said about it.

In the transverse section the prothallium in this species is more or less triangular like the prothallium of *Azolla filiculoides*. The side of the prothallium towards the base is the longest of the three sides.

The archegonium number found in the *Azolla filiculoides* prothallium is not equal to the number of archegonia found in *Azolla pinnata.* Often the number in *A. pinnata* far exceeds the number of *A. filiculoides.* The female prothallium of *A. Caroliniana* is much smaller in dimensions when compared with that of *A. pinnata.*

The prothallium of *A. pinnata* has evidently little power of independent growth ; however, it cannot be doubted that chlorophyll is developed in the prothallium to a little extent (M. P. No. 3).

Before showing signs of formation of archegonia, the prothallium grows more extensively than that of *A. filiculoides.*

The prothallium breaks open from the wall of the megaspore at the top in the direction towards the indusiate cap. This happens earlier than that described for *A. filiculoides.* The archegonium formation never begins when the prothallium is still enclosed in the megasporangium, but it begins when the prothallium is outside the wall of the megasporangium.

The development of archegonium formation runs along the usual lines. The youngest archegonium is found some distance back from the growing point. It seems that most of the superficial cells of the prothallium can be developed into archegonium mother-cells. We can compare this archegonium mother-cell formation favourably with that of *Marattia douglassi.*

The superficial archegonium mother-cell divides into a lower and an upper cell. The neck canal-cell of the archegonium is formed very early. It may be cut off from the central cell at the time when the first division takes place in the cover cell, or more often before the cover cell has divided (Figs. 1 and 2). The division between the neck canal cell and the central cell is not marked off by a cell wall. The ventral canal cell is not cut off before the cover cell is divided transversely into four cells. The ventral canal cell is not separated off from the ovum by a cell wall (Fig. 3).

The neck canal and the ventral canal cell are round when they are first cut off, but after that they become elongated in the direction parallel to the transverse axis of the prothallium (Fig. 3).

The oosphere is fairly big, at times very big, and is filled with protoplasm and has a big nucleus. As the oosphere attains maturity the nucleus becomes very distinct and considerably large. The chromosomes are very difficult to be made out. This may be compared to *Osmunda cinnamomea.* Sometimes more nucleoli than one are seen in the nucleus.

Basal cell is not observed in *Azolla pinnata.* Each row of the neck has four cells. The neck canal cell remains undivided.

Many neck canal cells are observed by Miss Lyon[8] in *Lycopodium annovitum* and *Lycopodium complanatum*. Only three neck canal cells are observed in Marattia. The neck canal nucleus present in *Botrychium Virginianum* and *Osmunda cinnamomea,* divides usually into two nuclei ; however these nuclei are not separated off from each other by a cell wall. There is a single neck canal cell in Marsilia. Thus the archegonium of *A. pinnata* comes nearest in this respect to that of Marsilia.

Fig. I.

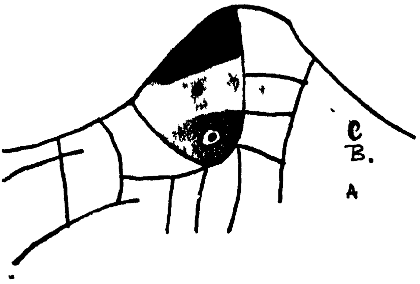


Fig. 2

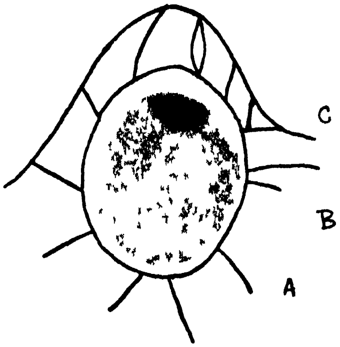


Fig. 3.

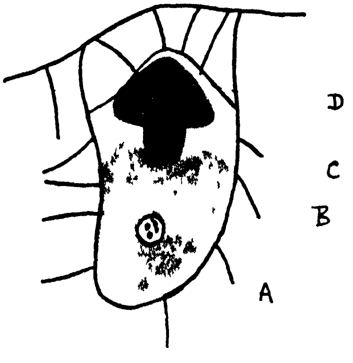


Fig. 4.

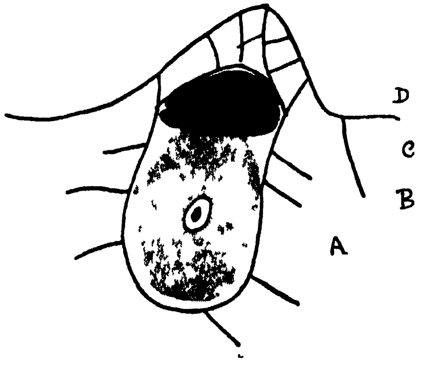


FIG. 1. Showing development of the archegonium. A. Central cell. B. Neck canal cell. C. Cover cell. Mag. × 750 times.

FIG. 2. Showing development of the archegonium. A central cell. B Neck canal cell. C Cover cell. Mag. × 750 times.

FIG. 3. Development of the archegonium. A. Ovum. B. Ventral canal cell. C. Neck canal ceil. D. Neck. Mag. × 750 times.

FIG. 4. Development of the archegonium. A. Ovum. B. Ventral canal cell. C. Neck canal cell. D. Neck. Mag. × 750 times.

Goebel[7] says, "It produces at first one archegonium and if the fertilization in one is effected, no more are produced. If no fertilization occurs other archegonium arises upto ten." I have found that a good number of archegonia are nearly always present and have never seen the first formed archegonium being fertilized. It is an exception than the rule that the first formed archegonium is fertilized and the general rule seems to be the formation of a number of archegonia before fertilization.

Fig. 5

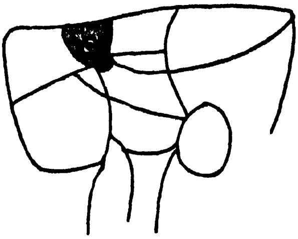


Fig 6

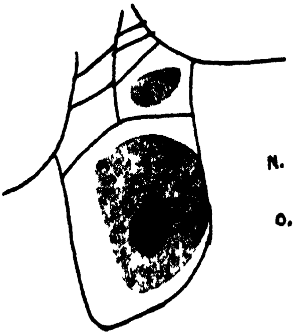
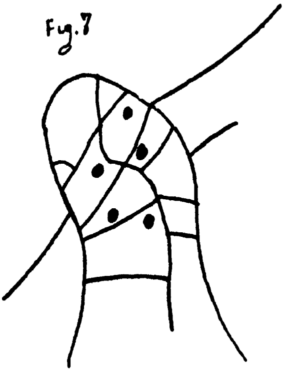


Fig 8.

Fig. 7



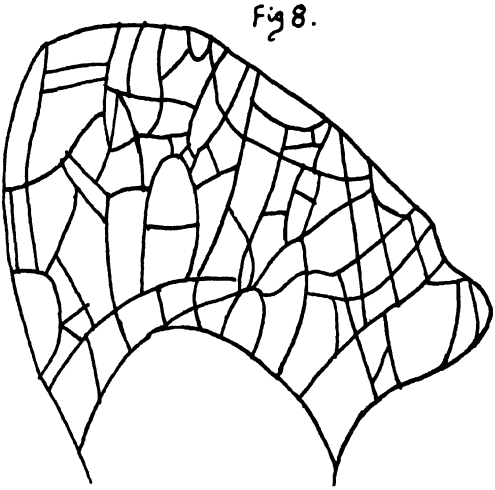


FIG. 5. Showing the mother cell of archegonium. Mag. × 435 times.

FIG. 6. Section through the archegonium. O. Ovum. N. Neck. Mag. × 750 times.

FIG. 7. Neck of the archegonium. Mag. × 750 times.

FIG. 8. Extensive prothallus Mag. × 435 times.

In very rare cases as many as thirty archegonia can be counted in a transverse section of a ripe prothallium of *A. pinnata*.

The central cell of the archegonium may be sometimes separated by from four to five layers of cells from the central spore cavity.

The second archegonium arises in close neighbourhood of the first. The oospheres of two archegonia are sometimes separated only by a single layer of cells from one another. The third archegonium arises near the first two. There is no definite sequence in the formation of the archegonia.

Discussion.—There is very little material for comparison. Campbell[5] has worked on the prothallium of *A. filiculoides*, but no other species of Azolla is worked out in detail as regards the female prothallium. Sud[12] thinks that the megasporangia germinate at the surface of water and produce a prothallium. He also says that the megasporangia sink if the oospheres in these are not fertilized. My observations show that this is not the case, and the megasporangia in which the oospheres are not fertilised remain at the bottom, and not that they sink to the bottom because no fertilization takes place. Thus in this respect our observations differ.

Sud's[12] statement as well as his figures about the formation of the prothallium in the lower part of the spore do not tally with the present observations. He says that prothallium completely fills the spore. It is very likely that what appears like a cell structure may be simply the granular condensations of the protoplasm.

Rao[10] states that when the prothallium is fully developed and the archegonia are formed the megasporangia come to the surface of water. Here also there is some difference. When the oosphere in the archegonium is fertilized and the embryo is formed, then alone with the help of the first formed leaves of the embryo and the float corpuscles the whole structure comes to the surface.

Rao also states that the megasporangia remain at the bottom during the summer and that they germinate after the rains.

This statement does not appear to be true at least for laboratory conditions. I have seen new sporophytes coming to the surface of water even in February and many more in March and April. It seems that there is no connection between rain and the germination of the new sporophyte. Rao[10] moreover states that the microsporangia and megasporangia are detached from the plants by about April when they float for some time and then sink. I have seen megasporangia and the microsporangia get detached even from December and by April new sporophytes have already germinated.

The usual number of archegonia in the prothallium is not considerable but it is true as Rao[10] has observed that sometimes we find as many as thirty archegonia.

I have tried to show how far the prothallium of *Azolla pinnata* resembles and how far it differs from that of *Azolla filiculoides.* The gradual retrogression of the archegonium with progressively advanced types of plants has long been proved. Azolla with its single canal nucleus in this species certainly points out for itself a fairly advanced position in Filicinae.

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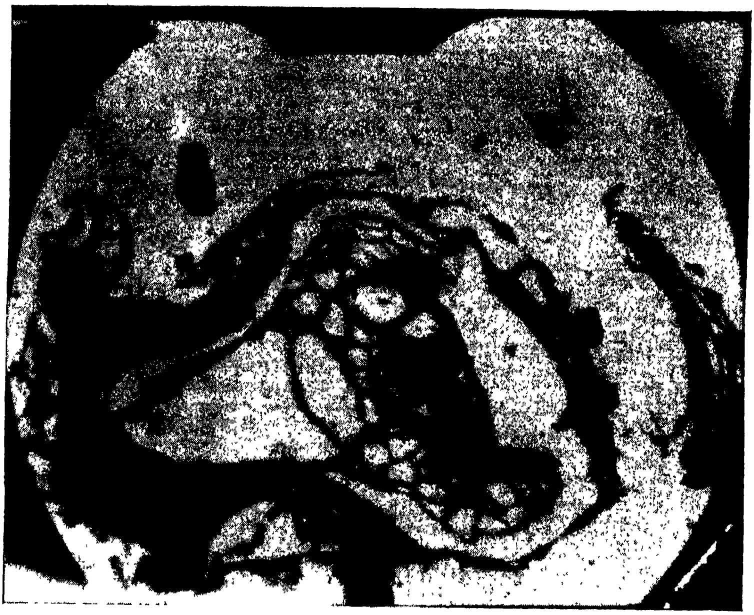
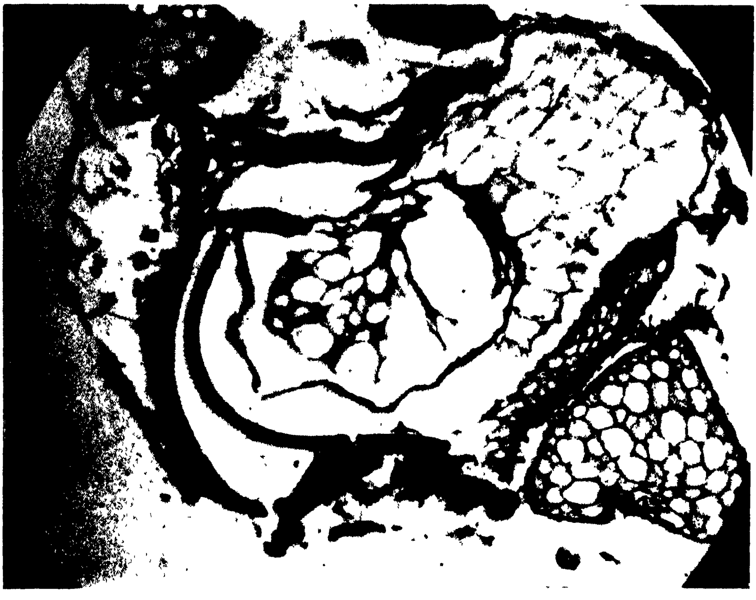
DRAWINGS

All drawings by Abbés camera lucida.



Microphotograph No. 1. Showing the lobed prothallium.



Microphotograph No. 2. Showing tissue formation in the vegetative part of the megaspore.

Microphotograph No 3 Showing the small quantity of chlorophyll in the prothallus

Microphotograph No 4 Showing the neck canal cell, the ventral canal cell and ovum of the archegonium

List of theses in Botany and Agriculture which have been accepted in lieu of the Examination for the degrees of M.Sc., M.Ag., and D.Sc., during the year 1937-38.

Subject.	Title of the thesis.	Name of the candidate.	Teacher.	Place of research.	Remarks.
Botany.	*Floral Organogeny and Structure and development of the micro- and megaspores and their gametophytes in Anona Squamosa and A. reticulata Linn.*	Mr. R. D. Adatia.	Prof. S. V. Shevade	Baroda College, Baroda.	
Do	*A contribution to the life-history of Gloeosporium sp. parasitic on Crinum Asiaticum Linn.*	Mr. O. T. Gandhi.	Prof. S. V. Shevade	Baroda College, Baroda.	
For the Degree of D.Sc.					
Agriculture.	*Nitrogen Recuperation and Fluctuations in the soils of the Bombay Presidency.*	Rao Bahadur D. L. Sahasrabudhe.		Poona.	
For the Degree of M.Ag.					
Do.	*Reclamation of Salt lands in the Deccan Canal Tracts.*	Mr. V. K. Gokhale.	Mr. C. C. Inglis, C.I.E. Executive Engineer, Irrigation Research Division, Poona.	Deccan Irrigation Circle, Poona.	
Do.	*Soil profile study of typical soils of the Bombay Deccan.*	Mr. R. P. Talati			

REVIEWS

A Course of Elementary Instruction in Practical Botany : By D. L. DIXIT, B.A., Professor of Botany, Fergusson College, Poona, assisted by P. V. SANE, Demonstrator in Biology, Fergusson College.

The author tells us in his preface that " this book is intended as a guide to college students preparing for Intermediate Science Biology examination." Easily available plants have been selected to illustrate all important points in external morphology and the plant types prescribed for detailed study in the old syllabus for the I.Sc. examination of the Bombay University have been fully dealt with. Detailed instructions are given regarding the materials and reagents to be used and the procedure to be followed in each of the practical lessons and occasionally, questions are suggested which would exercise the student's powers of observation and inference. The result has been the production of a very useful practical handbook.

We have, however, to note a few defects which may be remedied in a later edition of this book when this should appear. A number of typographical mistakes are left uncorrected in the " Errata." The advantage of bringing in studies in general morphology in the midst of the study of a type is doubtful and some confusion has been created by mixing up the two topics. The language and expression in some parts of the book leaves something to be desired in clarity and accuracy. For example, the brick-shaped cambium cells are described as " brick-like ", contiguous vascular bundles are referred to as " consecutive ", thick-walled cells are spoken of as " double-walled cells." The use of the new morphological terms " monosporangiate " and " bi-sporangiate " in place, respectively, of the older terms " unisexual " and " bisexual " in the description of flowers is evidently intended to emphasise the sexual character of the sporophylls which constitute the flower essentially, but there is danger of the terms conveying the meaning " with one sporangium and " with two sporangia " respectively.

These defects, however, do not seriously detract from the merits of the book as a whole which places Prof. Dixit's long experience as a teacher at the disposal of I.Sc. students and teachers. In a later edition which we hope the authors will soon require to bring out, they will have to add a few types to satisfy the requirements of the revised syllabus coming into force after the introduction of the Bifurcation scheme in the Bombay University. They may then also add the Indian names of plants in the other important vernaculars of the Bombay Presidency so as to extend its usefulness to a larger circle of students all over the Presidency.

S. L. A.

Hand-book of Physiology and Biochemistry. By the Late W. D. HALLIBURTON, M.D., LL.D., F.R.C.P., F.R.S. and R. J. S. McDOWELL, M.D., D.Sc., F.R.C.P. (Edin), 35th Edition. (Pp. 973, numerous illustrations in the Text, many of which are coloured, and four coloured plates. 18*s*. net.). London : John Murray, 1937.

This is one of the best known Text books in Physiology which has a long and noble history behind it. The new 35th Edition follows 2 years after the 34th, and has been ably revised by Professor McDowell. It has certain notable features. The title has undergone a change. For the first time it is called "Hand-book of Physiology and Biochemistry," Biochemistry being an addition. It is, as Professor McDowell rightly says, long overdue in a volume, which during Halliburton's authorship was a pioneer in such instruction, although he always preferred the term "Chemical Physiology." The insertion of blank pages at the end of each chapter, and of *dark* type of numbers, which it is useful to memorise, are features which will be helpful to the student. The portions of the book which have undergone special revision are those dealing with the humoural transmission of nerve impulse, Enzymes, Vitamins, Carbonic Anhydrase, Sex hormones, lymph formation, Pituitary gland, general metabolism and diet. This is a very good treatise on the subject and deservedly popular amongst the teachers and students. They will be happy to welcome the new edition.

S. L. B.

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EXCHANGES

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The Dean, College of Agriculture, Laguna P. I., University of the Philippines, Philippine Islands.

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Director of Archæology, Baroda State, Baroda.

Director, Institute of Educational Research, Sun Yatsen University, Canton, China.

Director, Malaria Institute of India, Kasauli, Simla Hills.

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† General Editor, Indian Science Abstracts, 1, Park Street, Calcutta.

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